Atomistic Modeling of Defects in Materials

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Atomic-Level Response of Materials to Irradiation Summer School

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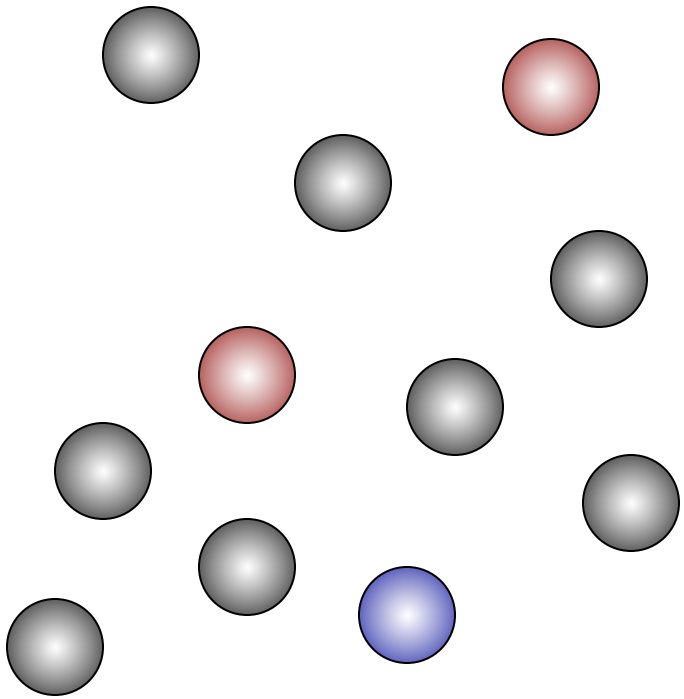
Acknowledgments

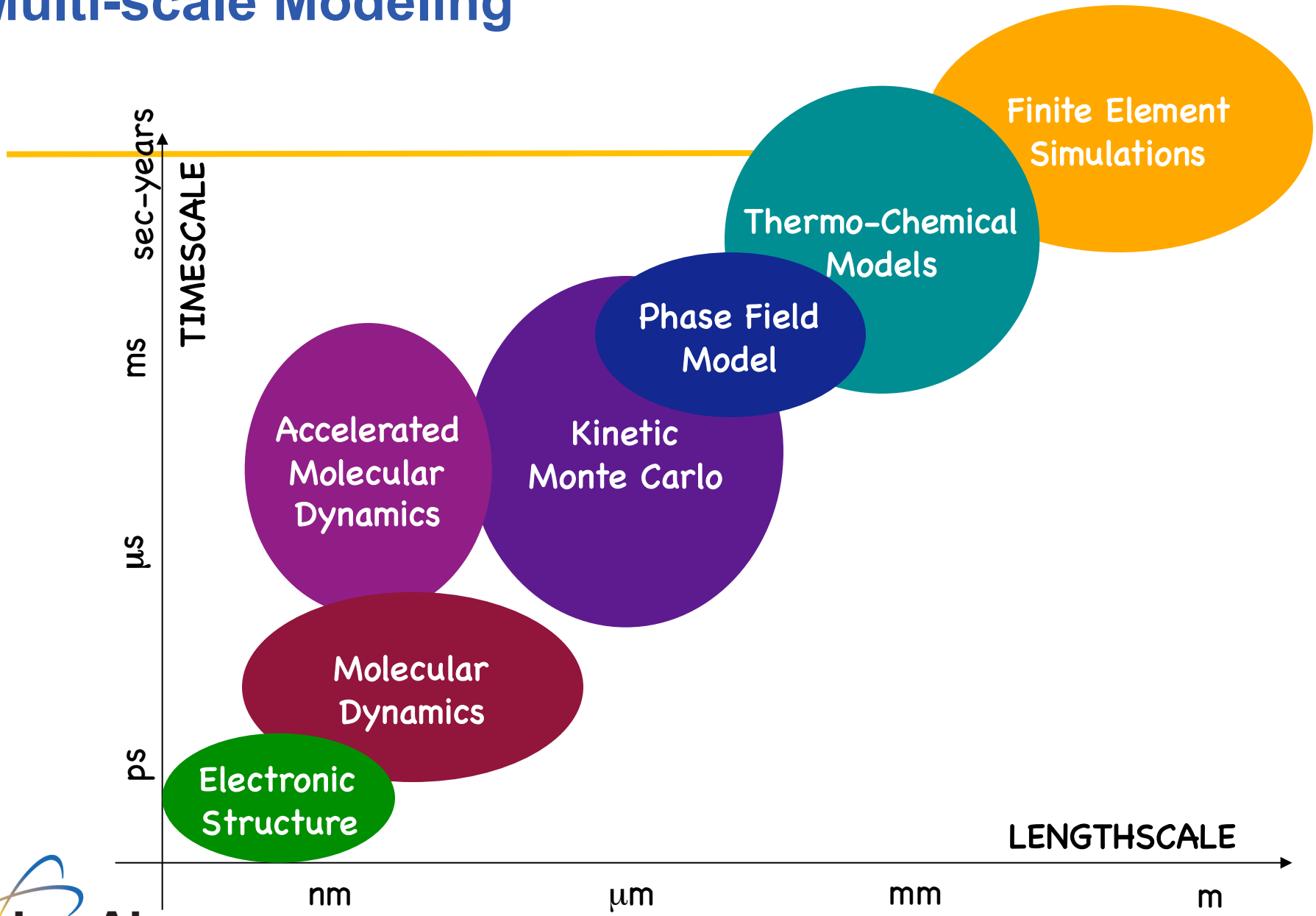
- Tim Germann
  - Gave similar lecture at last year's school in Santa Fe
- Art Voter
  - Provided slides on MD
- Graeme Henkelman
  - Provided slides on AKMC
- Wikipedia
  - Good basic summaries of many concepts

Atomistic methods: why?

- Given a collection of atoms:
  - What structure do they like to form?
  - What is their energy? Compared to other arrangements?
  - What will they do if heated up (what is their time evolution)?
- Atomistic methods can follow behavior of each atom explicitly
  - Extremely difficult experimentally



Multi-scale Modeling



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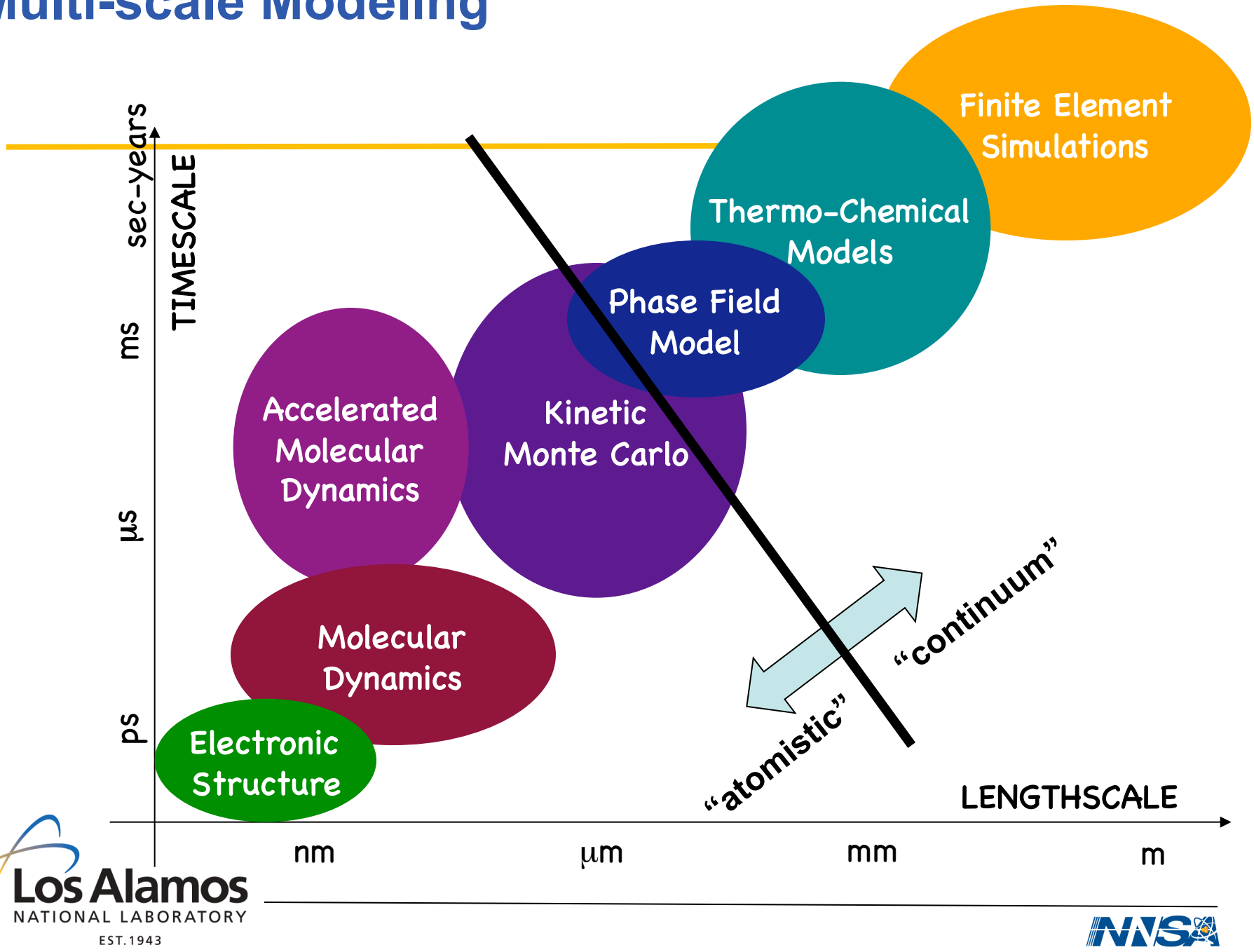
Multi-scale Modeling



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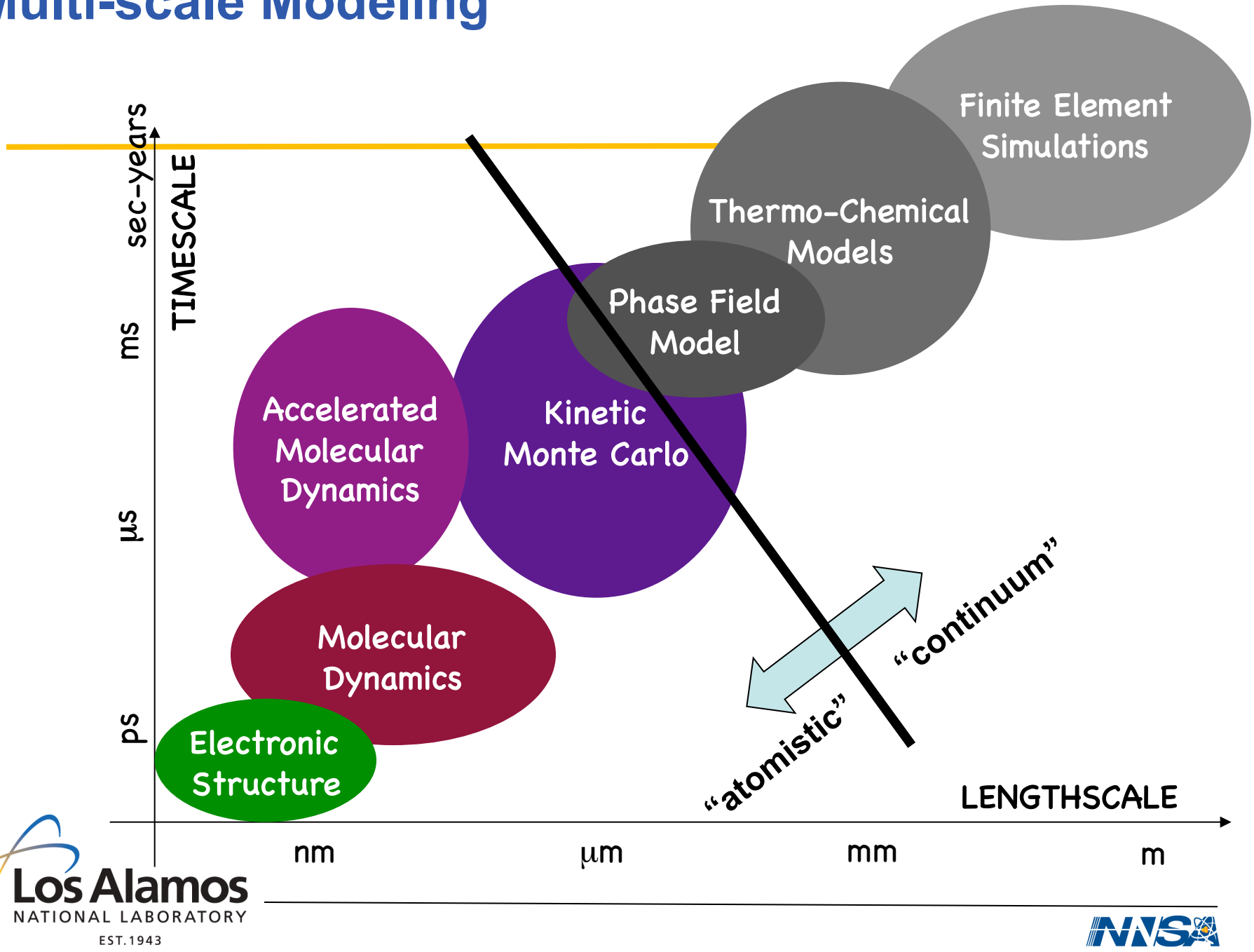
Multi-scale Modeling



Outline

I. Density Functional Theory

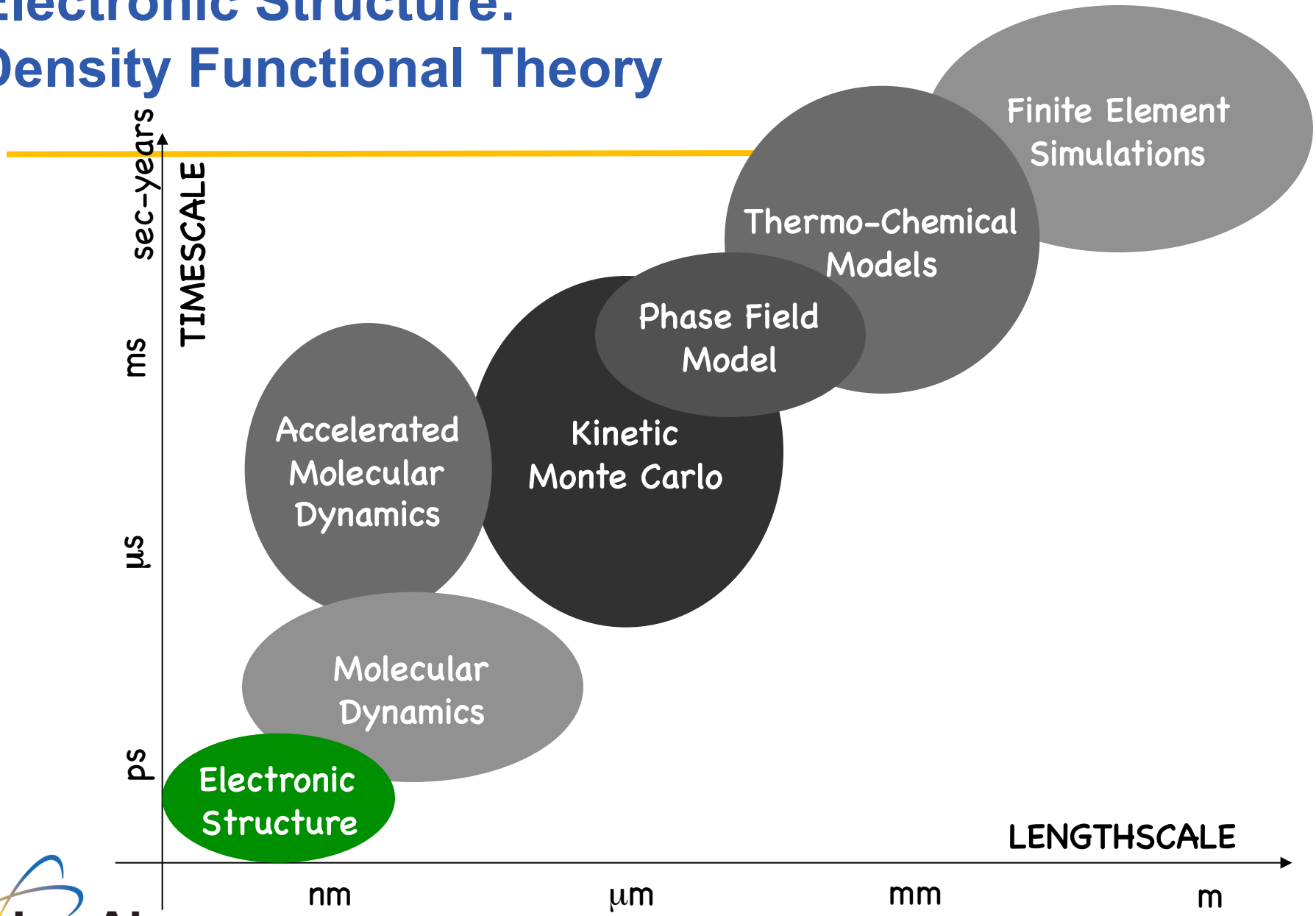
II. Molecular Dynamics

Interlude: The time scale problem

III. Accelerated Molecular Dynamics

IV. Kinetic Monte Carlo

Electronic Structure: Density Functional Theory



Density Functional Theory (DFT)

- ***Goal***: Given a set of atoms, determine their interaction
- Treat electrons explicitly → solve for electronic structure
  - Electronic structure dependent on atomic arrangement
  - Forces on atoms dependent on electronic structure

  → Solve self-consistently
- In principle, "ab initio" theory: no fitting, no information other than atomic position and species
  - In practice, some fits for convenience/necessity

The origins of DFT: Hohenberg-Kohn Theorems

- *Theorem 1 (uniqueness):* The ground-state electron density $\rho(\mathbf{r})$ uniquely determines the external potential $V_{ext}(\mathbf{r})$ (the potential due to the ions).

The origins of DFT: Hohenberg-Kohn Theorems

- *Theorem 1 (uniqueness):* The ground-state electron density $\rho(\mathbf{r})$ uniquely determines the external potential $V_{ext}(\mathbf{r})$ (the potential due to the ions).
- *Theorem 2 (variational principle):* For any positive definite trial density $\rho_{tr}(\mathbf{r})$ that satisfies

$$\int \rho_{tr}(\mathbf{r})\, d\mathbf{r} = N$$

then

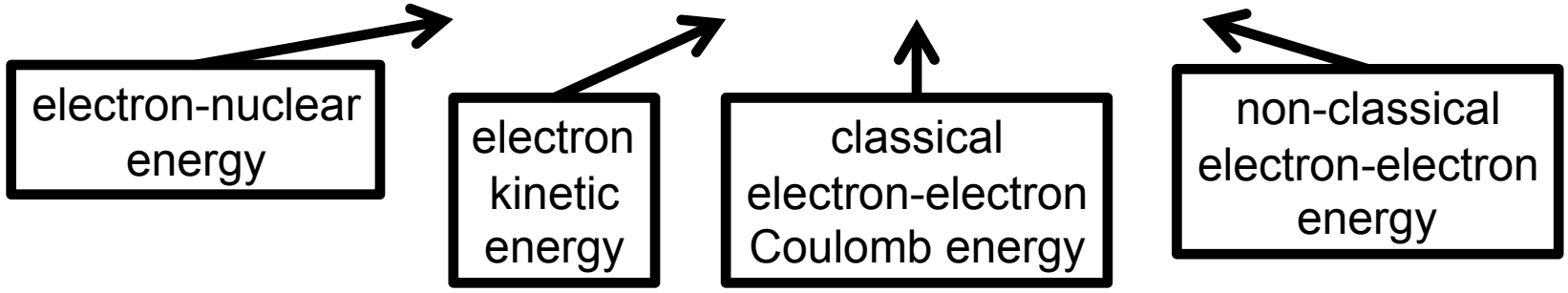
$$E\left[\rho_{tr}(\mathbf{r})\right] = F\left[\rho_{tr}(\mathbf{r})\right] + \int \rho_{tr}(\mathbf{r}) V_{ext}(\mathbf{r})\, d\mathbf{r} \geq E_0$$

- There thus exists a *universal* density functional $F[\rho(\mathbf{r})]$.

DFT Energy

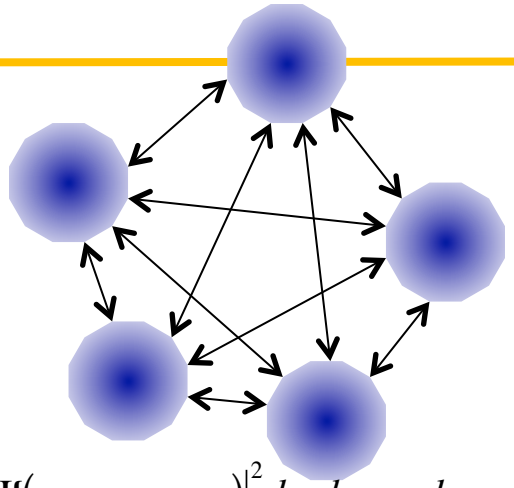
- Total energy of the system can be expressed as

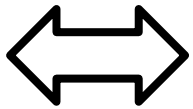
$$E[\rho] = E_{Ne}[\rho] + T[\rho] + J[\rho] + E_{ncl}[\rho]$$

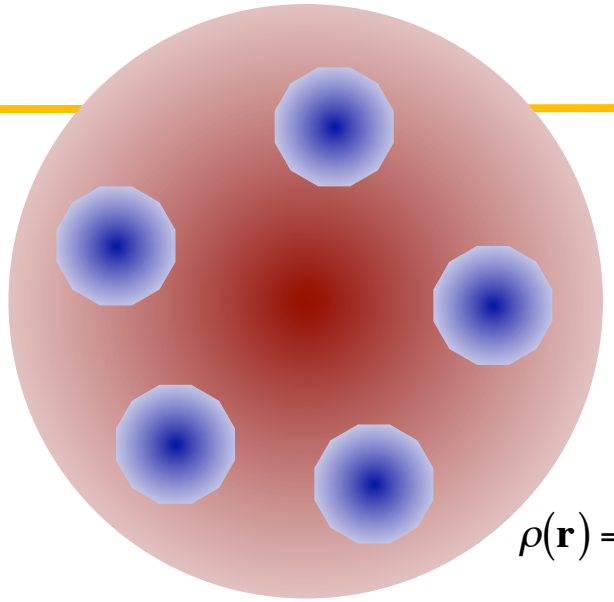


  - Of the three electron-electron terms, only *J* known exactly

Kohn-Sham Equations







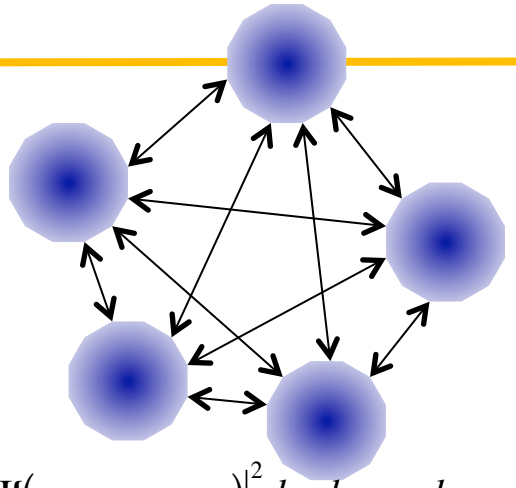
$$\rho(\mathbf{r}) = N \int \cdots \int \left|\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\right|^2 d\mathbf{x}_1 d\mathbf{x}_2 \ldots d\mathbf{x}_N$$

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \left|\psi_i(\mathbf{r})\right|^2$$

fully-interacting
N-electron system

system of *N* independent, non-interacting electrons embedded in effective potential

Kohn-Sham Equations



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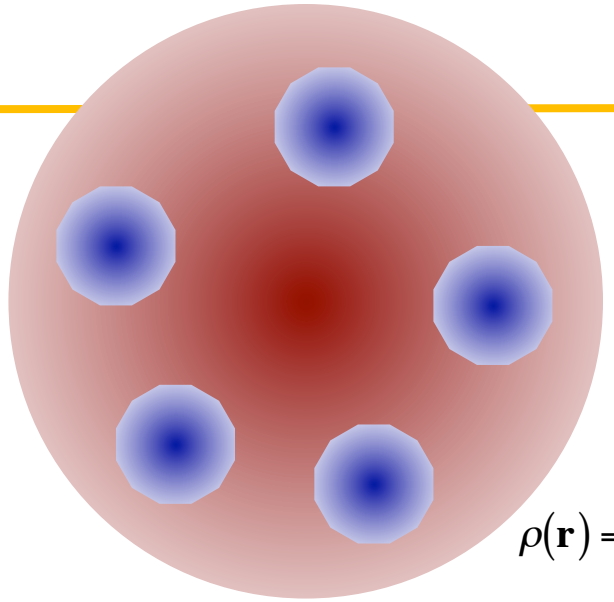


$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \left|\psi_i(\mathbf{r})\right|^2$$

system of *N* independent, non-interacting electrons embedded in effective potential

- The Kohn-Sham equations

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

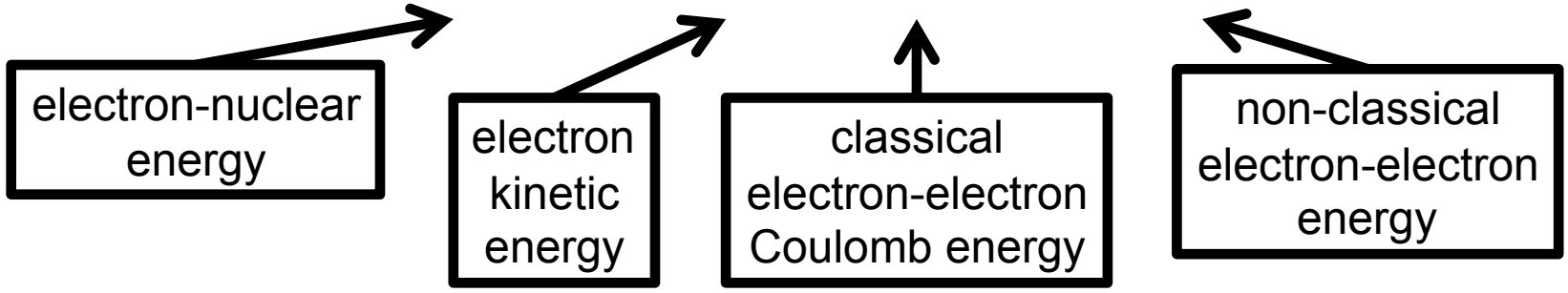
are solved for the *N* orthonormal Kohn-Sham orbitals $\psi_i(\mathbf{r})$.

$$\left\langle \psi_i \middle| \psi_j \right\rangle = \delta_{ij}$$

DFT Energy

- Total energy of the system can be expressed as

$$E[\rho] = E_{Ne}[\rho] + T[\rho] + J[\rho] + E_{ncl}[\rho]$$



  - Of the three electron-electron terms, only *J* known exactly

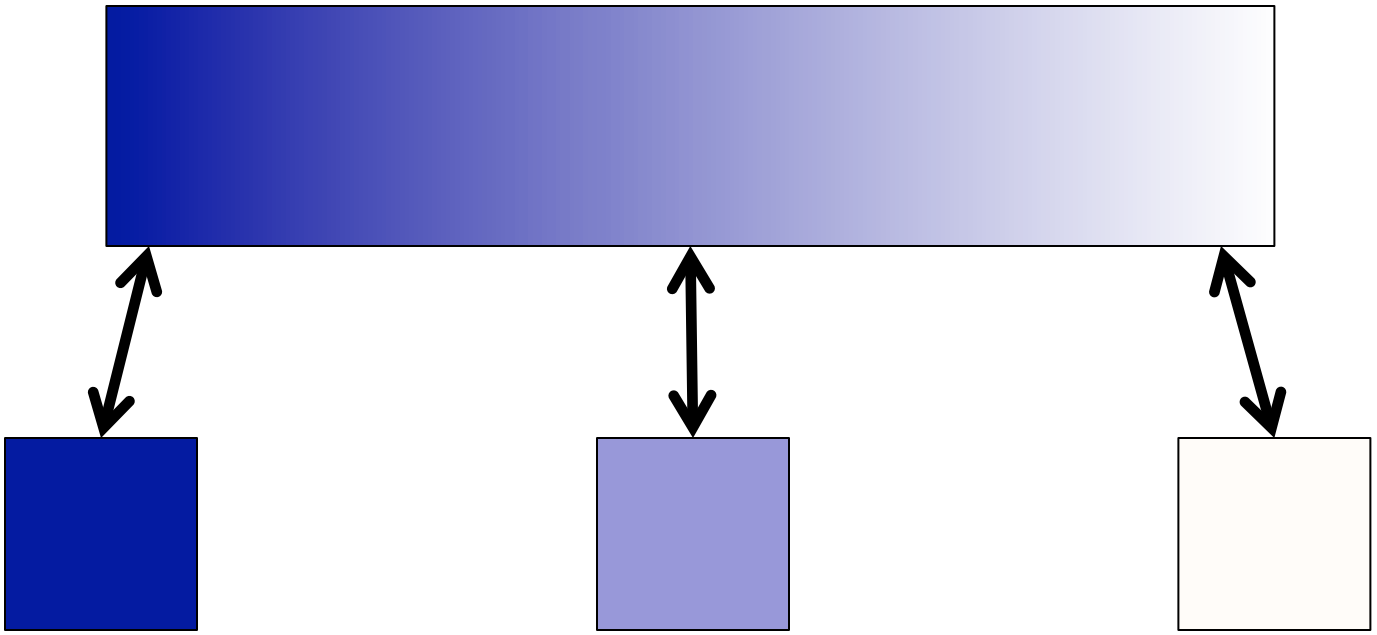
- Kohn-Sham energy:

$$E[\rho] = E_{Ne}[\rho] + T_s[\rho] + J[\rho] + E_{xc}[\rho]$$

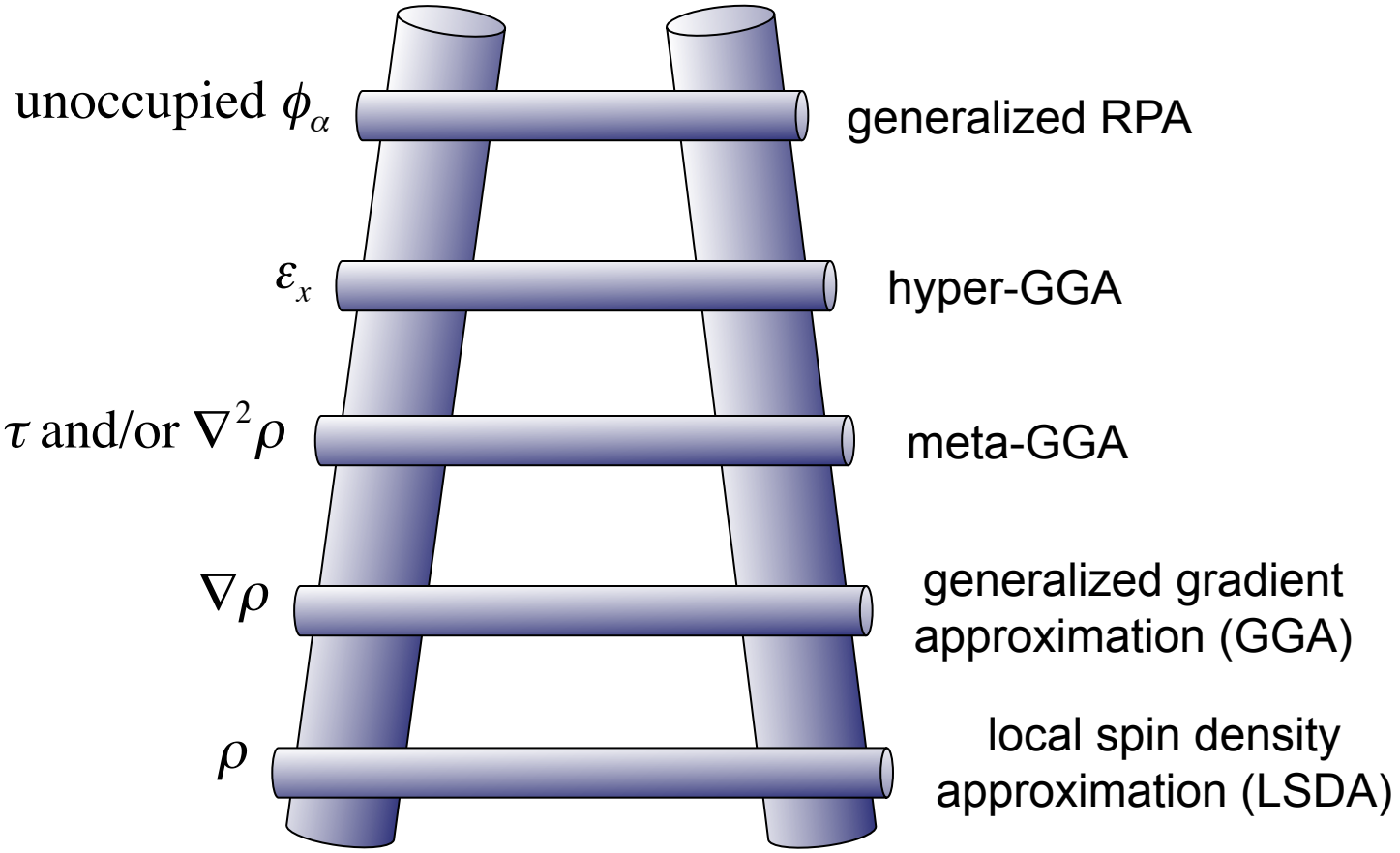
  - Now, T_s *also* known exactly, only E_{xc} not known (but approximated)

Local Density Approximation

$$E_{xc}[\rho] \approx E_{xc}^{uniform-electron-gas}[\rho]$$



"Jacob's Ladder" of Exchange-Correlation Functionals



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Perdew et al, JCP **123**, 062201 (2005)

Basis Sets

- Local orbitals, e.g. Linear Combination of Atomic Orbitals (LCAO)
  - Most appropriate for finite molecular systems (quantum chemistry community)
  - Quasi-religious: Gaussian vs. Slater-type orbitals, Pople vs. Dunning basis sets, ...
- Plane waves
  - Most suitable for periodic systems with delocalized (metallic) bondings
  - Simplified basis set convergence criterion: kinetic energy cutoff E_{cut}
- "Muffin tin" hybrid approaches, e.g. the Linearized Augmented Plane Wave (LAPW) method
  - Partitions the calculation supercell into an atomic-like sphere around each atom, and plane waves for the remaining "interstitial" region

Brillouin zone sampling

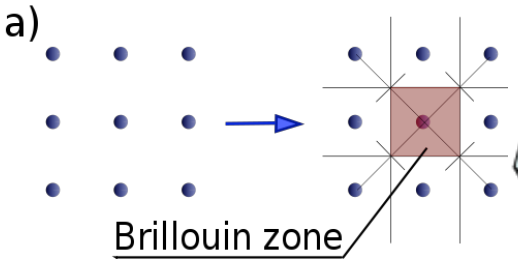
- Eigenfunctions of a periodic system must satisfy Bloch's theorem:

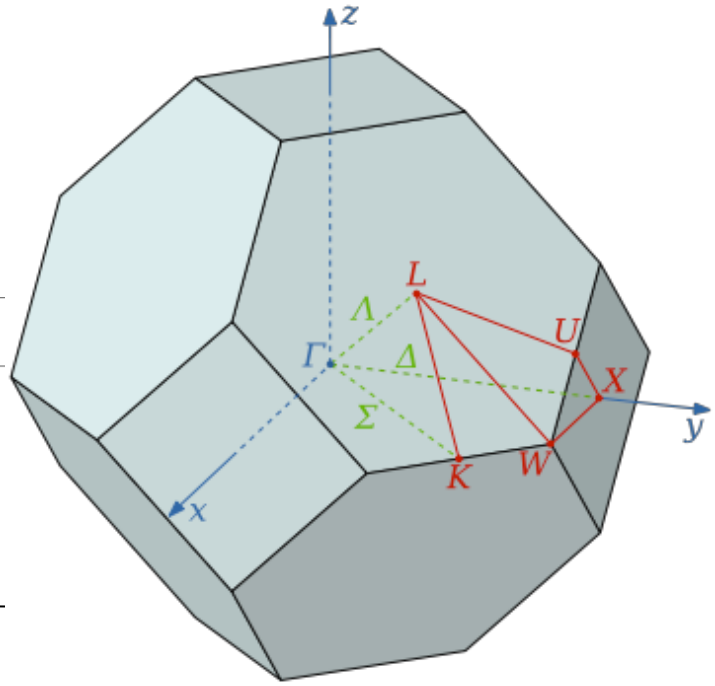
$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$$

- We can thus replace an infinite volume integral (over periodic images of a supercell) with one over the 1st Brillouin zone in k-space and discretize:

$$\int_{\Omega} d\Omega \Rightarrow \int_{\mathbf{k}} d\mathbf{k} \approx \sum_{\mathbf{k}} w_{\mathbf{k}}$$

- Single k-point (Γ) often used, may be sufficient if:
  - Little/no interaction between supercells
  - Supercell is large
  - System is disordered





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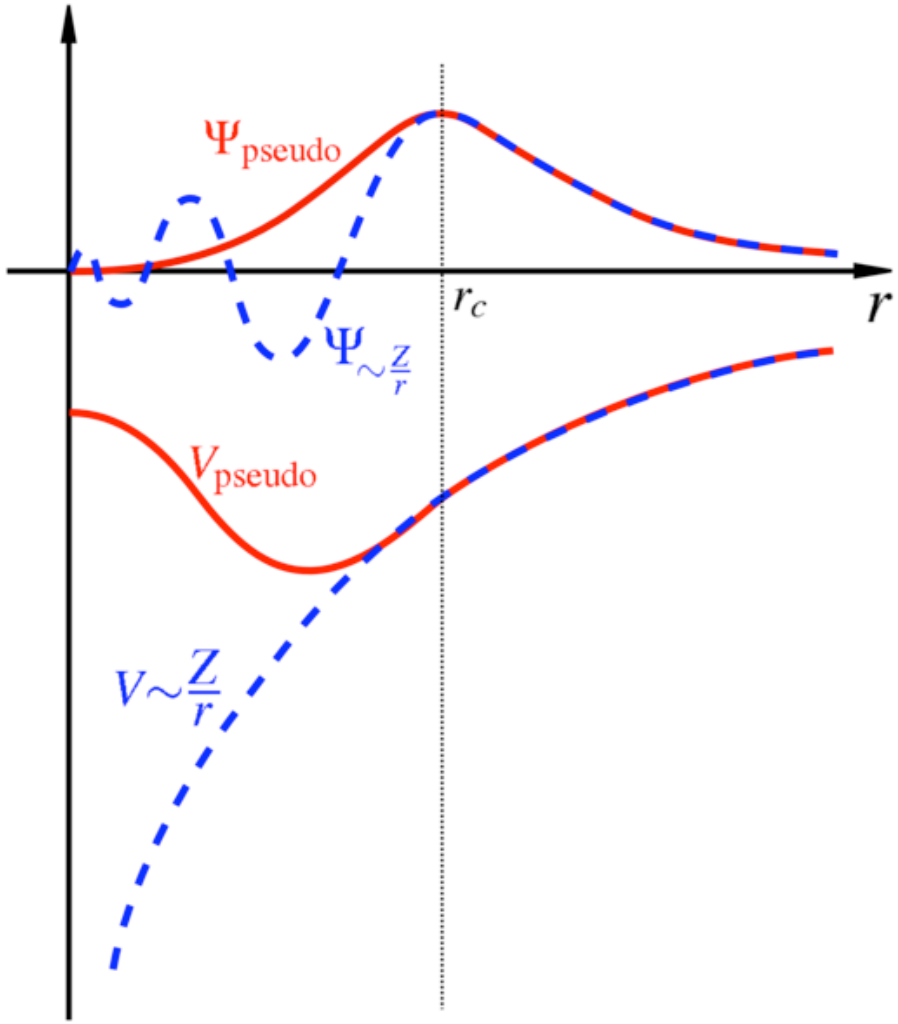
Pseudopotentials

- Replace complicated effects of the core (i.e. non-valence) electrons of an atom with an effective potential, or pseudopotential
  - Has the same potential, and electron density, for r > rc.
- Motivation:
  - Reduction of basis set size
  - Reduction of number of electrons
  - Inclusion of relativistic and other effects

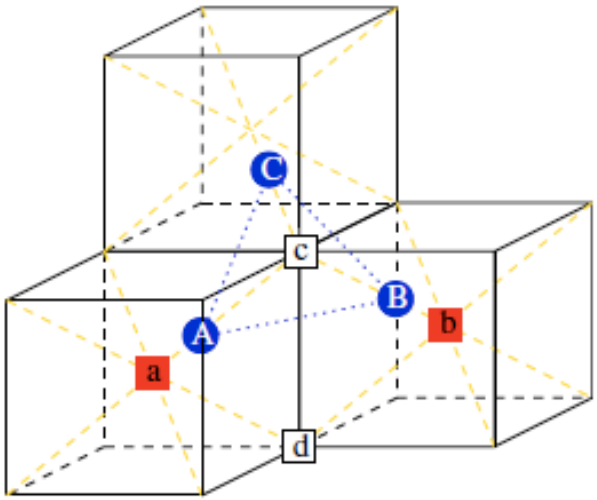


Popular plane wave-pseudopotential DFT codes

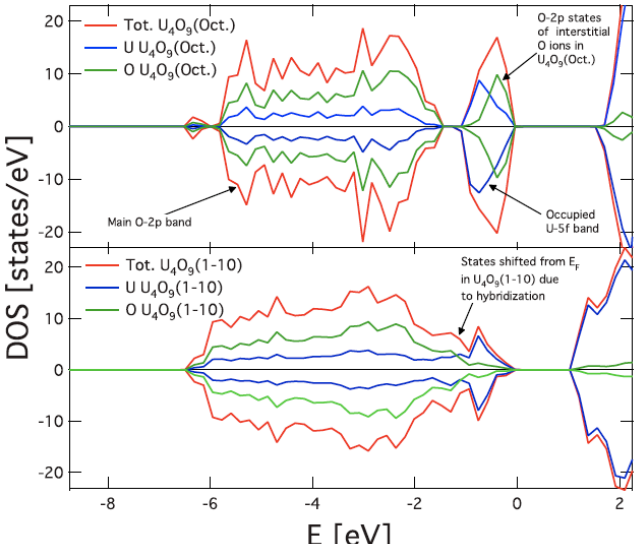
- VASP (Vienna Ab-initio Simulation Package)
  - http://cms.mpi.univie.ac.at/vasp/
- ABINIT
  - http://www.abinit.org/
- Quantum ESPRESSO
  - http://www.quantum-espresso.org/
- SIESTA
  - http://www.icmab.es/siesta/index.php

Defect properties that can be calculated with DFT

- Defect structure and energies
  - Relative stability of different structures
  - Formation/solution/incorporation energies
  - Migration energies
- Phase stability
- Electronic structure of defects
  - Charge transfer
  - Hybridization
  - Electronic defect states in gap
- …



Di-interstitial structures in UO_2. Split structure is 0.25 eV lower in energy than "Willis" structure.



Electronic structure of U_4O_9 built based on Willis (top) and split (bottom) di-interstitial structures.

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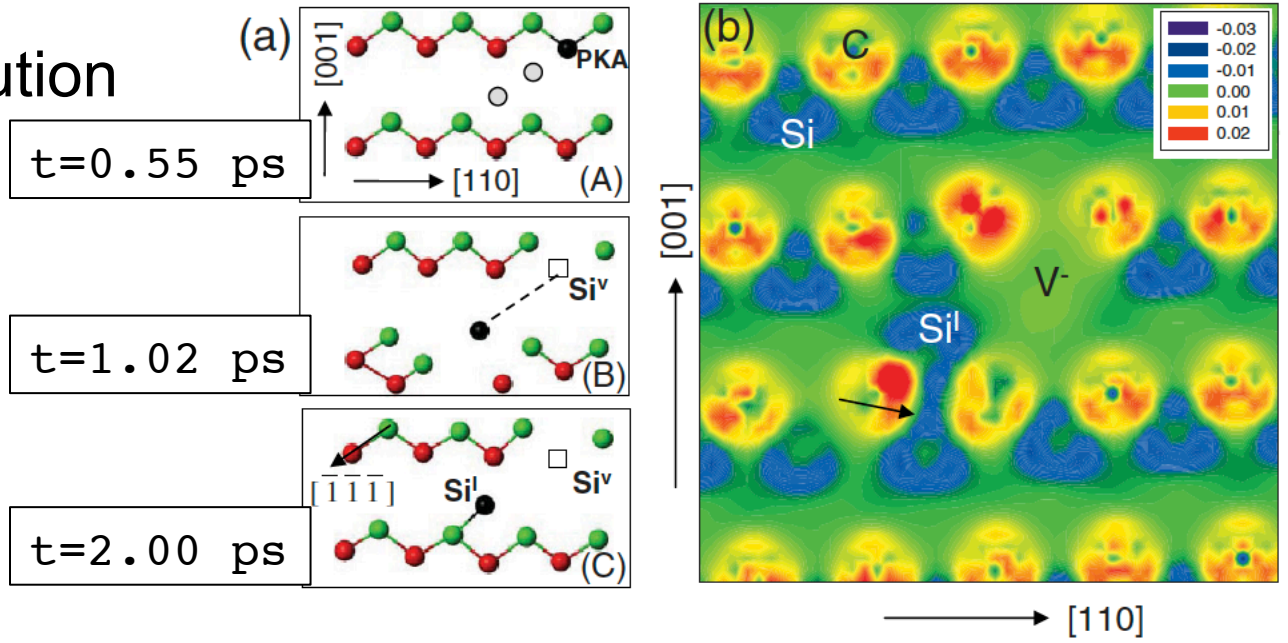
DFT in Radiation Effects Studies: Role of Charge Transfer

Gao et al, PRL **103**, 027405 (2009)

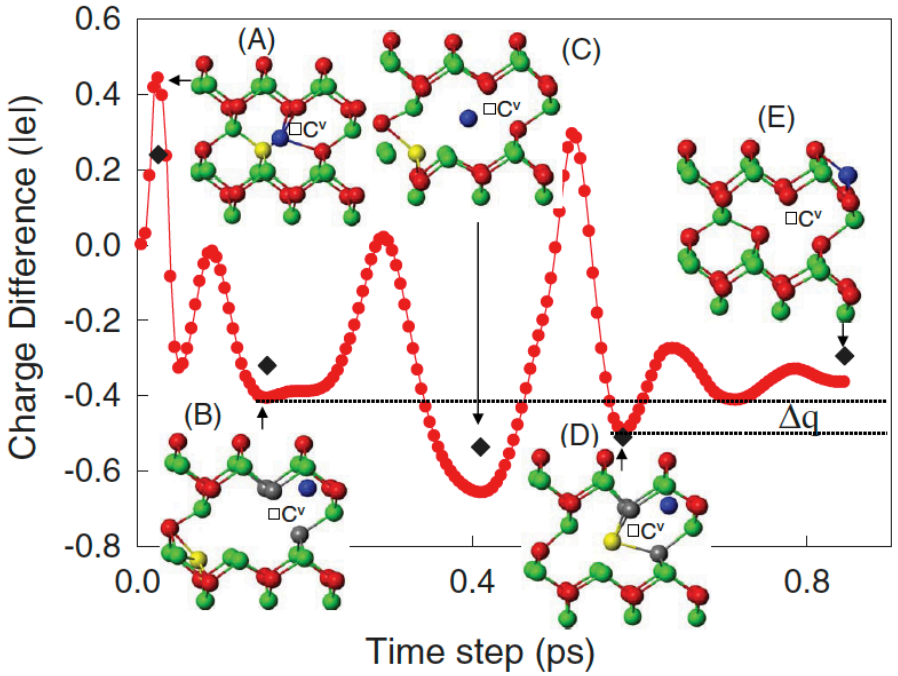
- Use DFT to simulate a collision cascade
  - Usually realm of classical MD
- Si primary knock-on atom (PKA) leads to formation of V_{Si} and Si_i
- Charge distribution varies significantly amongst atoms

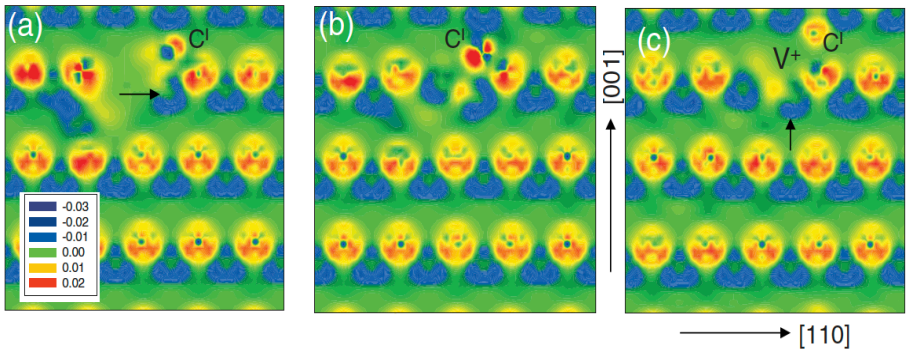


DFT in Radiation Effects Studies: Role of Charge Transfer

Gao et al, PRL **103**, 027405 (2009)

- Carbon PKA
- Charge of PKA varies significantly as cascade evolves
  - +0.4/-0.6 electrons
- V_C and C_i formed
- Charge varies amongst other atoms in system





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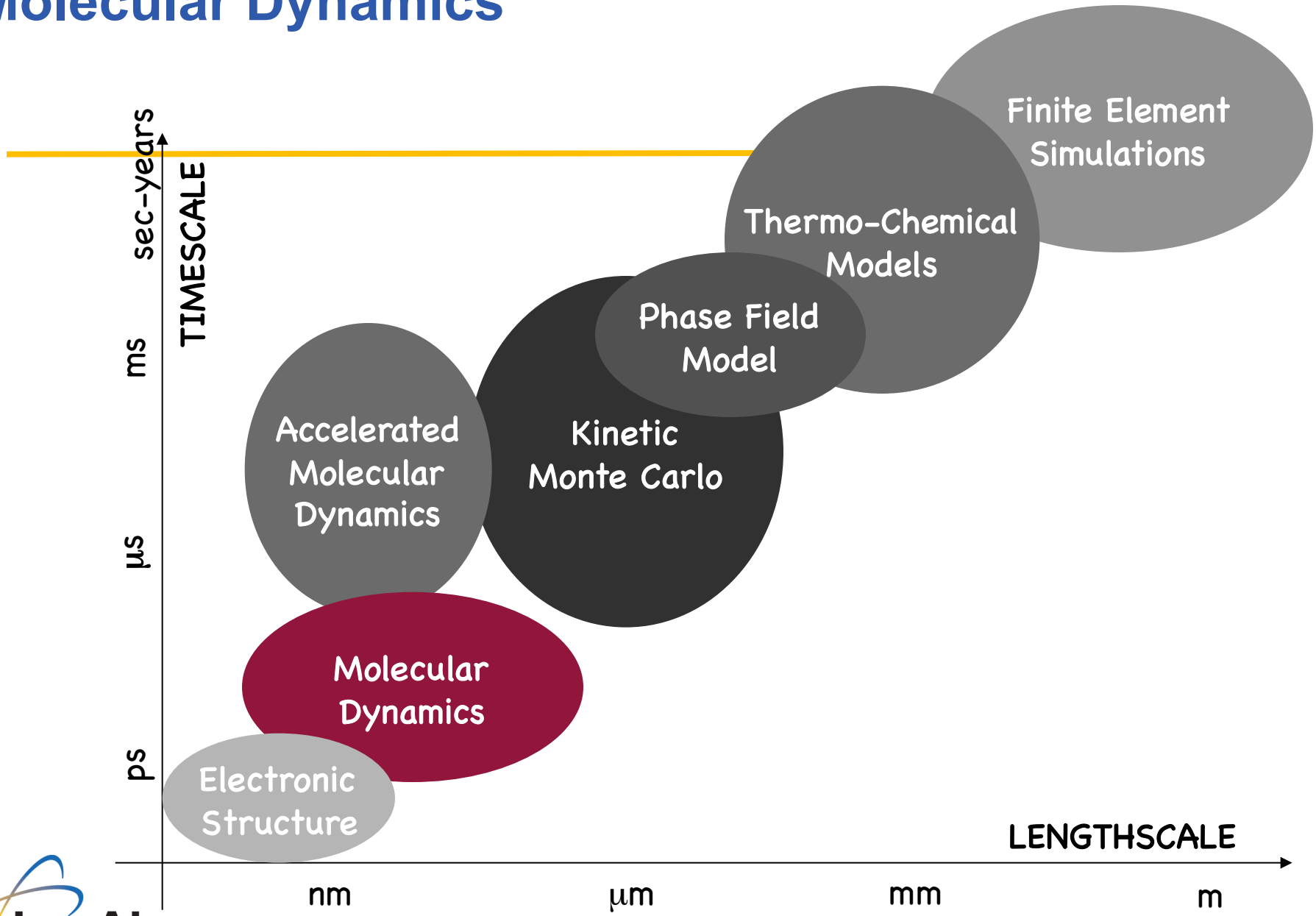
Factors affecting accuracy and precision

- Accuracy
  - Exchange-correlation functional
  - System size
  - Relaxation
  - Boundary conditions
- Precision
  - Pseudopotential
  - *k*-point sampling
  - Basis set

Active (and challenging!) areas of research

Molecular Dynamics



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Molecular Dynamics

- ***Goal***: Given a collection of atoms, what is their time evolution
- Integrate Newton's 2nd law:

$$\mathbf{F}=m\mathbf{a}$$

- Integration requires knowing force **F**:

$$\mathbf{F}=-\delta V/\delta \mathbf{x}$$

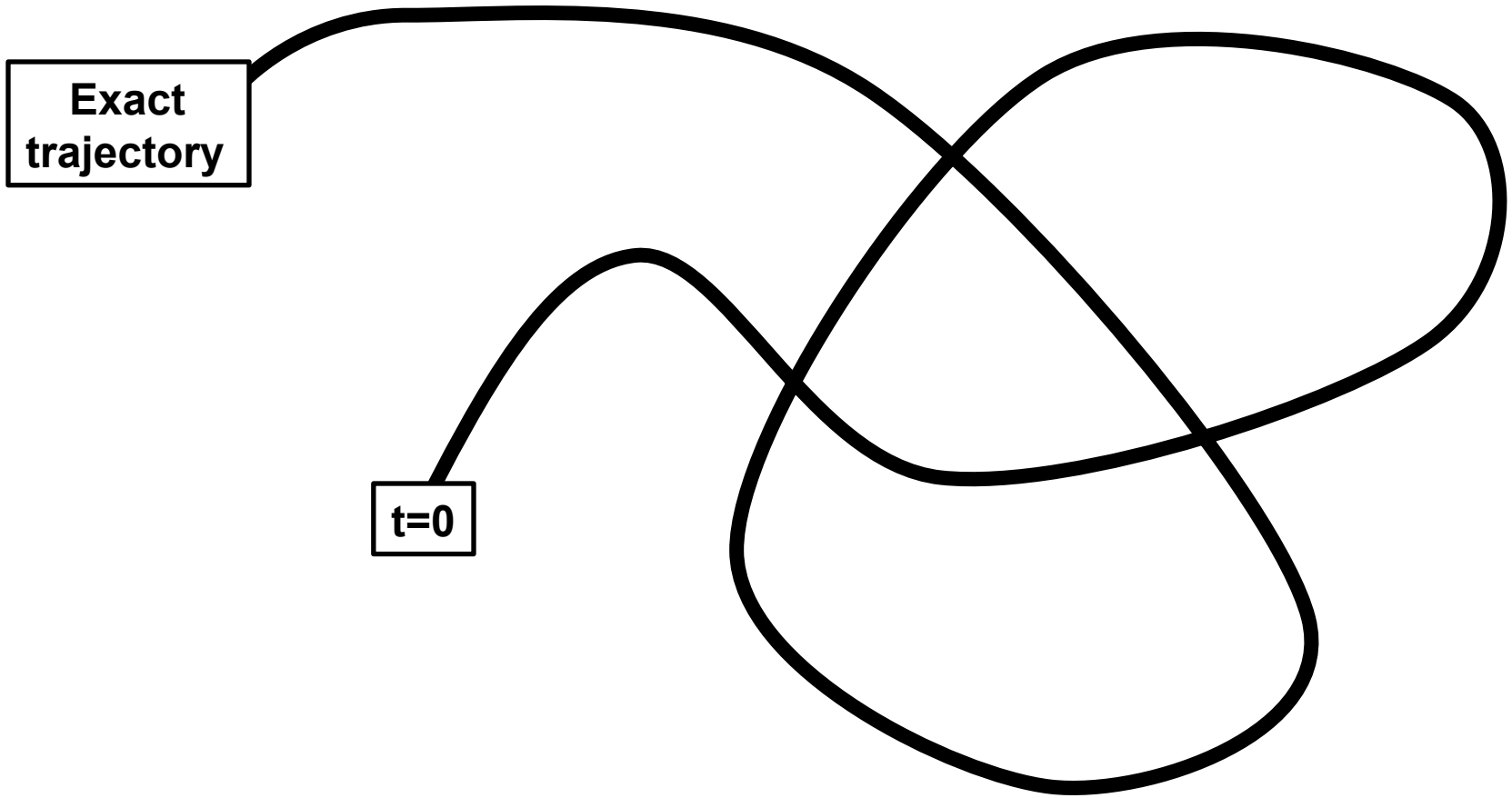
- Accurate integration requires small time steps

$$\Delta t \sim 1\text{-}5 \text{ fs}$$

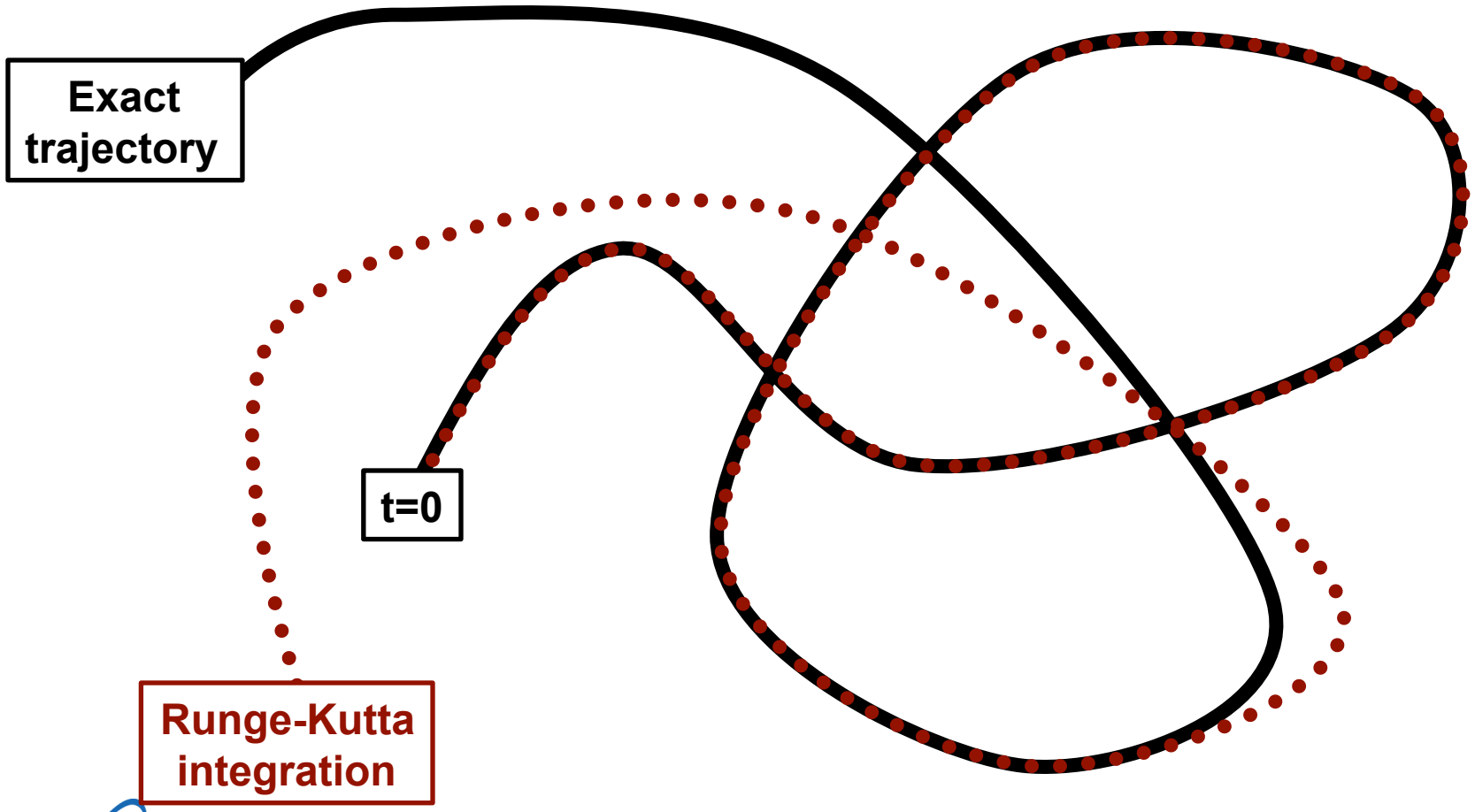
- Total simulation times:

$$t \sim 1\text{-}1000 \text{ ns}$$

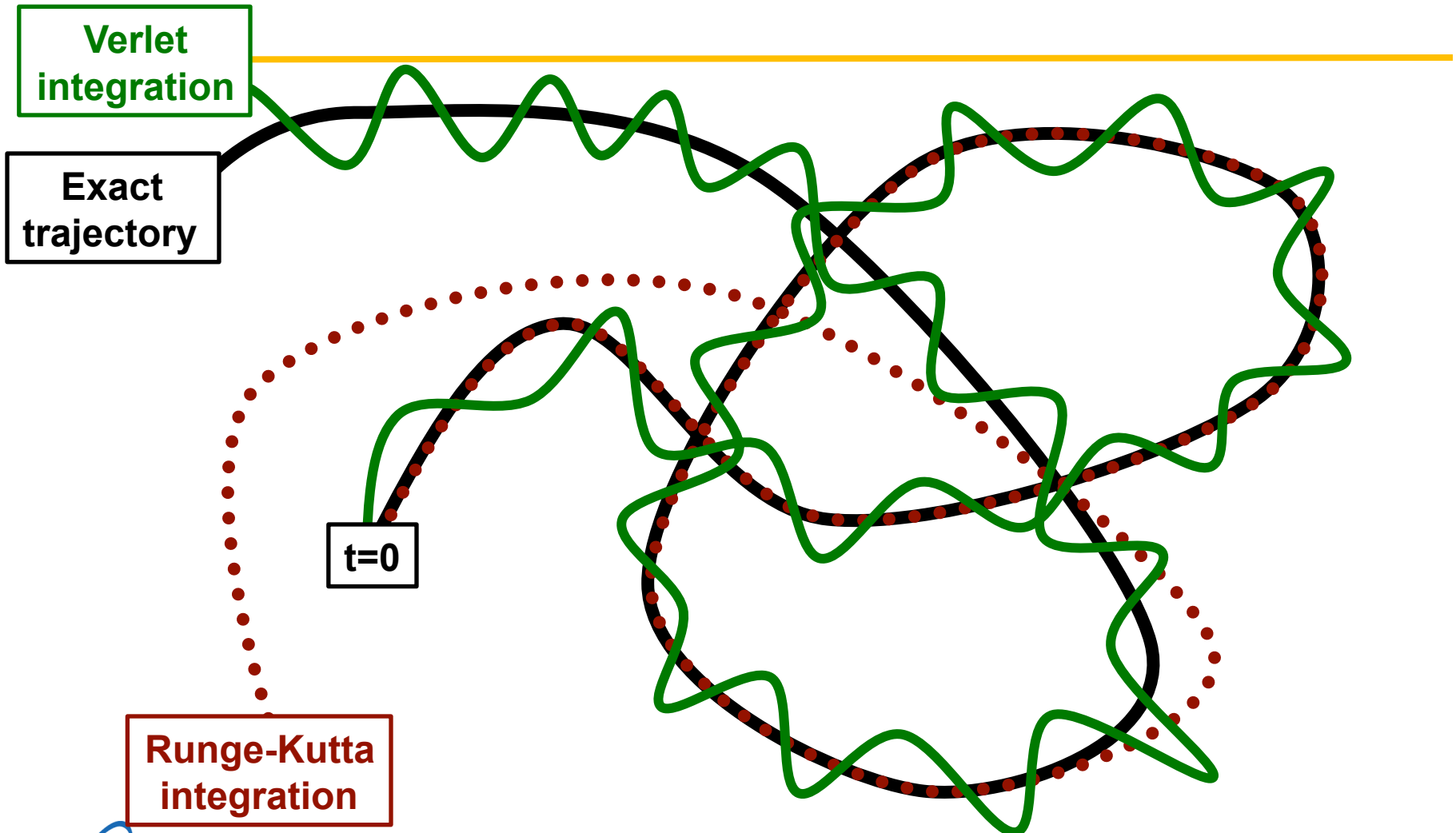
Integrating F=ma



Integrating F=ma



Integrating F=ma



Interatomic Potentials

- Integration of Newton's 2nd law requires knowing force **F**:

$$\mathbf{F}=-\nabla V$$

- Primary challenge of MD is determining a good potential V for the system of interest
  - (Semi-) Empirical functions fit to experimental or DFT data
- Potentials can be classified into three primary categories, depending on type of bonding
  - Metallic
  - Covalent
  - Ionic

Potentials for Metals

- Lennard-Jones
  - Used primarily for noble gases, simple metals

$$E_i = \frac{1}{2}\sum_j \phi(r_{ij}) = \frac{1}{2}\sum_j 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

- Embedded Atom Method (EAM)
  - Derived from density functional theory ideas
  - Embedding function *F* accounts for "electron density" ρ of neighbors → many body effects
  - Works very well for fcc metals
  - Daw & Baskes, PRB **29**, 6443 (1984)

$$E_i = \frac{1}{2}\sum_j \phi(r_{ij}) + F\left[\sum_j \rho(r_{ij})\right]$$

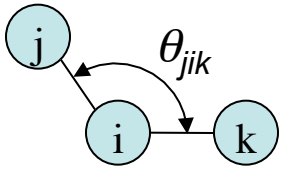
- Modified Embedded Atom Method (MEAM)
  - Angular terms add screening effects between atoms
  - Treats more complex metals (e.g. Sn, Pu) and non-metals
  - Baskes, PRB **46**, 2727 (1992)

$$E_i = \frac{1}{2}\sum_j \phi(r_{ij}) + F\left[\sum_j \rho(r_{ij}) + \text{angular terms}\right]$$

Potentials for Covalent Materials (Semiconductors)

- Stillinger-Weber
  - Explicit function of angle between triplets of atoms θ_{jik}
  - Primarily Si

$$E_i = \frac{1}{2}\sum_j \phi\left(r_{ij}\right) + \sum_{j,k} f\left(\theta_{jik}\right)$$



- Bond-order (Tersoff)
  - Primarily for group IV elements (C, Si, Ge)
  - Pair terms
  - B_{ij} is the bond-order and depends on number of bonds, bond lengths, and bond angles to neighbors of the i-j pair
  - Basis for Brenner, REBO, AIREBO (C and hydrocarbons)

$$E_i = \frac{1}{2}\sum_j \phi_R\left(r_{ij}\right) + \frac{1}{2}\sum_j B_{ij}\phi_A\left(r_{ij}\right)$$

Potentials for Ionic Systems (Ceramics)

- Buckingham potential

$$E_i = \tfrac{1}{2}\sum_j \left[A_{ij} e^{\left(-r_{ij}/\rho_{ij}\right)} - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right]$$

  - Exponential accounts for short range repulsion
  - *C* term is van der Waals
  - Electrostatics due to charges *q* on ions
    - Full or partial charges
    - Rigid or polarizable ions
    - Computationally demanding, needs methods such as Ewald, fast multipole, Wolf summation…

- Morse term

$$\phi_{ij} = D\left(1 - e^{-a\left(r_{ij} - r_e\right)}\right)^2$$

  - Added to Buckingham potential to account for covalency between some ions
  - Basak potential for UO_2 (Basak et al, J Alloys & Compounds 360, 210 (2003))

UO_2 potentials

Govers, et al, JNM **366**, 161 (2007).

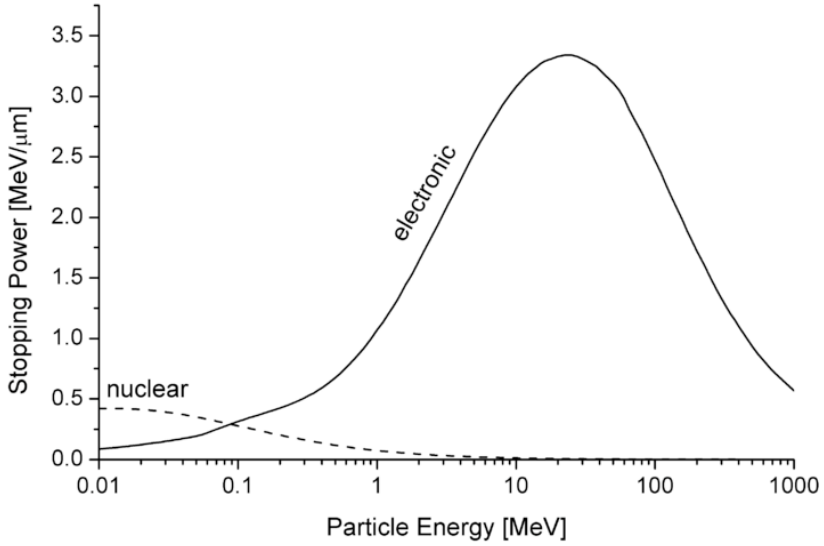
- Extremely large number of parameterizations, mostly based on Buckingham potential

Table 4
Properties calculated with the different potentials for spheres radii in the Mott–Littleton method of 9 and 20 Å

	Units	Potentials																		
		At.1 [43]	Bas. [42]	Bus. [9]	Ca.1 [6]	Ca.2 [6]	Gri. [28]	Ja.1 [14]	Ja.2 [14]	Kar. [23]	Le.a [12]	Le.b [12]	Le.c [12]	Me.1 [44]	Me.2 [45]	Mor. [24]	Sin. [20]	Th.1 [4]	Wal. [10]	Yam. [35]	Exp. or ab initio [3,49–71,74–77]
$E_{coh.}$	eV	103.0	43.2	104.5	103.1	94.5	105.7	103.1	103.5	100.6	103.6	103.6	103.6	99.9	100.8	65.9	100.8	103.0	104.1	45.6	
a_0	Å	5.454	5.454	5.468	5.451	5.521	5.462	5.448	5.452	5.466	5.389	5.390	5.382	5.559	5.469	5.447	5.449	5.410	5.328	5.467	5.4552 (extrapol.)
C_{11}	GPa	479.8	408.1	532.1	420.1	434.4	524.2	421.2	398.4	369.3	427.0	426.8	426.9	432.3	389.2	217.1	370.7	472.8	471.0	419.5	389.3
C_{12}	GPa	101.9	61.2	122.3	125.7	100.4	147.3	126.5	132.4	87.8	121.5	121.4	119.3	77.9	118.6	79.0	86.3	96.4	102.6	59.4	118.7
C_{44}	GPa	95.5	59.5	118.8	66.2	57.3	89.2	66.8	73.8	70.3	119.4	88.5	49.9	24.2	59.6	78.4	65.6	84.3	89.4	54.7	59.7
B	GPa	227.9	176.9	258.9	223.8	211.8	272.9	224.9	221.0	181.6	223.3	223.2	221.8	196.0	208.8	125.0	181.1	221.9	225.4	179.4	204.0
E	GPa	444.3	392.2	486.4	362.2	396.7	459.6	363.3	332.4	335.6	373.2	373.0	374.8	408.6	333.8	174.9	338.1	440.1	434.3	404.7	385.0
ν		0.18	0.13	0.19	0.23	0.19	0.22	0.23	0.25	0.19	0.22	0.22	0.22	0.15	0.23	0.27	0.19	0.17	0.18	0.12	
ε		11.1	4.0	18.4	20.9	25.4	13.1	20.8	19.8	18.4	9.9	17.8	17.5	23.1	24.0	10.2	20.1	13.7	14.4	3.8	24.0
ε_∞				6.2	5.4	5.2	5.3	5.4	5.8			5.4	5.4	2.6	5.3						5.3
Phonons at Γ																					
T. mode	cm^{-1}	260.5	289.4	183.3	273.7	235.8	343.9	274.8	287.8	198.4	282.6	274.0	271.4	194.3	245.1	221.1	190.0	235.9	235.1	294.7	280.0
L. mode	cm^{-1}	493.6	577.1	282.2	444.9	447.1	533.2	446.9	434.6	381.6	443.4	400.7	396.6	411.3	413.2	287.7	377.4	473.5	457.5	616.2	450.0
Formation energies																					
O FP_{oo}	eV	6.9	6.0	6.4	5.1	5.1	6.9	5.2	4.9	4.9	6.8	5.4	5.3	4.0	4.6	3.9	4.7	6.2	6.0	6.0	3.6–3.9[a]
OFP1[b]	eV	5.6	5.2	5.5	3.7	3.7	5.8	3.7	3.9	3.8	5.5	4.2	4.0	Rec.	1.3	3.1	3.6	5.0	4.8	5.2	3.63[a]
OFP2[b]	eV	5.5	4.8	5.5	[d]	4.1	5.8	4.3	4.0	3.8	5.4	4.4	4.2	[d]	3.1	3.0	3.5	4.9	4.8	4.7	3.1–5.4
UFP_{oo}	eV	24.5	17.0	22.4	18.8	16.7	24.1	19.0	19.2	19.5	25.5	20.4	19.2	17.7	18.6	15.7	19.0	22.4	22.3	18.5	9.5–12.6[a]
UFP[b]	eV	6.4	12.4	[d]	14.5	13.0	18.7	14.8	14.7	15.1	[d]	15.9	14.5	13.4	15.8	11.9	[d]	17.2	16.4	13.9	8.5–9.6, 6.09[a]
$Sch._{oo}$	eV	10.2	10.8	10.8	9.8	7.4	13.4	10.0	11.1	7.0	12.6	9.8	9.2	4.2	9.7	8.0	6.3	8.1	8.3	13.5	4.9–6[a]
Sch.1	eV	4.8	5.4	6.2	5.4	4.1	7.3	5.5	6.4	3.4	6.2	5.4	4.6	1.3	5.5	4.1	3.0	3.6	3.8	7.9	4.1[a]
Sch.2	eV	4.5	5.7	5.7	4.9	4.2	7.0	5.1	6.0	3.0	6.0	5.6	4.2	0.7	5.0	3.9	2.5	3.3	3.5	8.2	4.23[a]
Sch.3	eV	5.0	6.5	5.5	4.6	4.8	7.2	4.7	5.6	3.0	6.5	6.3	4.3	0.8	4.3	4.2	2.5	3.6	3.7	9.2	6–7
Migration energies																					
O_i mig	eV	0.7	1.3	0.8	[c]	3.6	1.1	0.7	0.5	0.5	0.2	[c]	[c]	0.1	0.7	0.7	0.1	0.5	0.3	1.3	0.9 – 1.3
O_i mig2	eV	0.7	1.3	0.8	[d]	[c]	1.1	0.7	0.8	0.3	0.2	[d]	[d]	.4	0.7	0.7	0.1	0.5	0.4	1.3	
V_O mig	eV	0.3	0.3	0.3	0.5	0.3	0.7	0.6	0.6	0.1	0.5	0.5	0.5	0.2	0.5	0.3	0.1	0.2	0.2	0.4	0.5
U_i mig	eV	[c]	5.1	1.3	4.2	3.7	[d]	4.4	[d]	[c]	1.8	1.3	5.2	[d]	1.3	4.2	3.2	[c]	4.4	5.1	4.4–5.6
U_i mig2	eV	6.5	6.4	[d]	4.4	3.7	[d]	4.9	[d]	[d]	7.2	9.6	5.2	2.2	4.5	4.2	[d]	3.1	5.6	3.9	4.4–5.6
V_U mig	eV	5.6	5.7	8.2	3.7	3.1	6.8	5.2	0.6	3.9	6.2	4.4	2.8	3.7	4.5	3.9	0.9	5.7	5.2	6.4	
Binding energies																					
$2V_O$	eV	−2.5	−2.6	−1.8	−1.4	−1.4	−2.2	−1.4	−1.3	−1.8	−2.5	−1.7	−1.9	−2.2	−1.2	−1.5	−1.7	−2.3	−2.2	−2.9	
$V_O + V_U$	eV	3.0	3.0	2.4	2.3	1.8	3.3	2.4	2.5	1.9	3.5	2.4	2.5	1.5	2.2	2.1	1.7	2.4	2.5	3.2	0.4[a]
$2O_i$	eV	−0.8	−1.0	−0.1	[d]	0.6	−0.8	−0.2	−0.4	0.0	−1.3	−0.6	−0.6	0.4	−0.3	−0.9	0.3	−0.4	−0.4	−1.0	
$2O_i$[b]	eV	−0.8	−1.0	0.0	[d]	0.7	−0.7	−0.1	−0.4	0.0	−1.3	−0.7	−0.6	−17.9	−0.2	−0.9	0.1	−0.2	−0.3	−0.9	
4-vac.	eV	7.6	7.5	6.9	6.6	5.0	9.2	6.7	7.2	5.0	9.0	6.5	6.5	3.7	6.4	5.6	4.6	6.2	6.1	8.0	

Additional considerations for irradiation simulations

- High-energy collisions ("nuclear stopping"): Ziegler-Biersack-Littmark (ZBL) universal repulsive potential
  - Important for close approach during collisons
- Magnetic materials, e.g. ferritic steels
- Electronic stopping $S_e(E)$: Firsov theory, TRIM/SRIM code
- Electron-phonon coupling: two-temperature models



Nordlund & Dudarev, C. R. Physique **9**, 343 (2008).

Ensembles

- Microcanonical: NVE
  - Constant energy
- Canonical: NVT
  - Constant temperature
  - Thermostat (e.g. Langevin) coupling to an external heat bath
  - Damping (friction) constant γ_i
  - Stochastic (noise) term **R**

$$m_i \dot{\mathbf{v}}_i = \mathbf{F}_i - m_i \gamma_i \mathbf{v}_i + \mathbf{R}$$

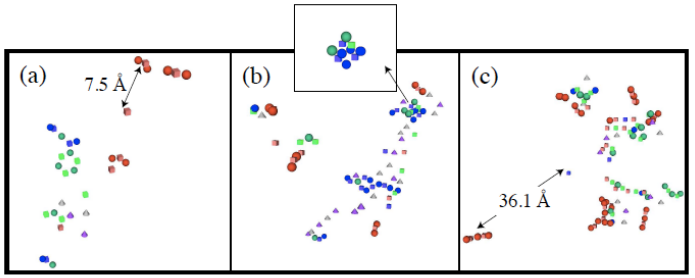
- Constant-pressure (NPT)

Popular MD codes for materials

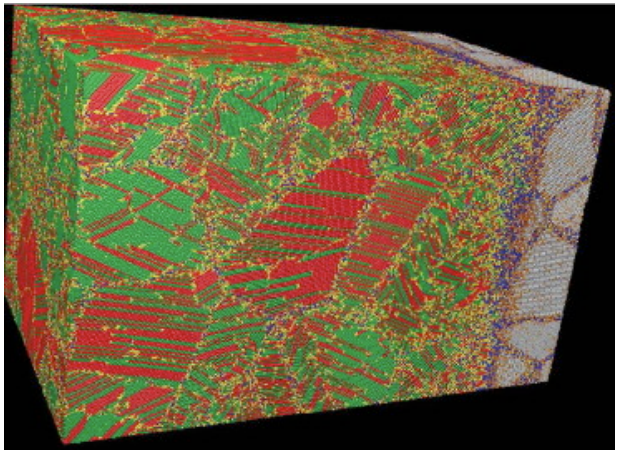
- LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator)
  - http://lammps.sandia.gov/
- IMD (ITAP Molecular Dynamics program)
  - http://www.itap.physik.uni-stuttgart.de/~imd/index.html
- SPaSM (Scalable Parallel Short-range Molecular dynamics)
  - Primarily an internal LANL code

Defect properties that can be calculated with MD

- Ensemble averages
  - Density
  - Pair distribution function
  - Time correlations
  - …
- Diffusion coefficients
- Thermal conductivity
- Collision cascades
- Grain boundary structure
- …



Defect structures formed after 2 keV PKA in spinels (MgB_2O_4) with different levels of inversion.



Dislocation structure in shocked nc-Fe, courtesy Germann and Kadau. 1 trillion atom simulations now possible.

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One of the very first applications of MD: Collision Cascades

PHYSICAL REVIEW VOLUME 120, NUMBER 4 NOVEMBER 15, 1960

Dynamics of Radiation Damage*

J. B. Gibson, A. N. Goland,† M. Milgram, and G. H. Vineyard
Brookhaven National Laboratory, Upton, New York

(Received July 14, 1960)

Radiation damage events at low and moderate energies (up to 400 ev) are studied by machine calculations in a model representing copper. Orbits of knock-on atoms are found and the resulting damaged configurations are observed to consist of interstitials and vacancies. Thresholds for producing permanently displaced atoms (i.e., interstitials) are about 25 ev in the ⟨100⟩ direction, 25 to 30 ev in the ⟨110⟩ direction, and around 85 ev in the ⟨111⟩ direction. Collision chains in the ⟨100⟩ and ⟨110⟩ directions are prominent; at low energies the chains focus, at higher energies they defocus. Above threshold, the chains transport matter, as well as energy, and produce an interstitial at a distance. The range of ⟨110⟩ chains has been studied in detail. Localized vibrational modes associated with interstitials, agitations qualitatively like thermal spikes, ring annealing processes, and a higher energy process somewhat like a displacement spike have been observed. Replacements have been found to be very numerous.

The configurations of various static defects have also been studied in this model. The interstitial is found to reside in a "split" configuration, sharing a lattice site with another atom. The crowdion is found not to be stable, and Frenkel pairs are stable only beyond minimum separations, which are found to be very much dependent on orientation.

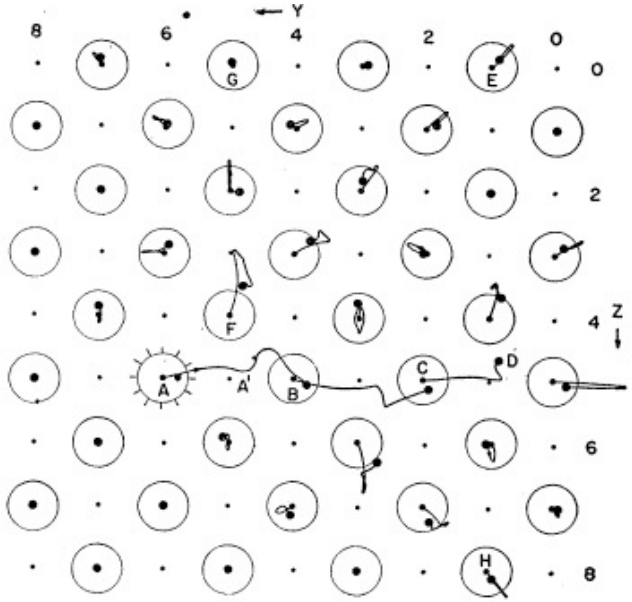

FIG. 6. Atomic orbits produced by shot in (100) plane at 40 ev. Knock-on was at A and was directed 15° above $-y$ axis. Large circles give initial positions of atoms in plane; small dots are initial positions in plane below. Vacancy is created at A, split interstitial at D. Run to time 99. (Run No. 12).

Cover of *J. Appl. Phys.* **30** (8) (1 Aug 1959)

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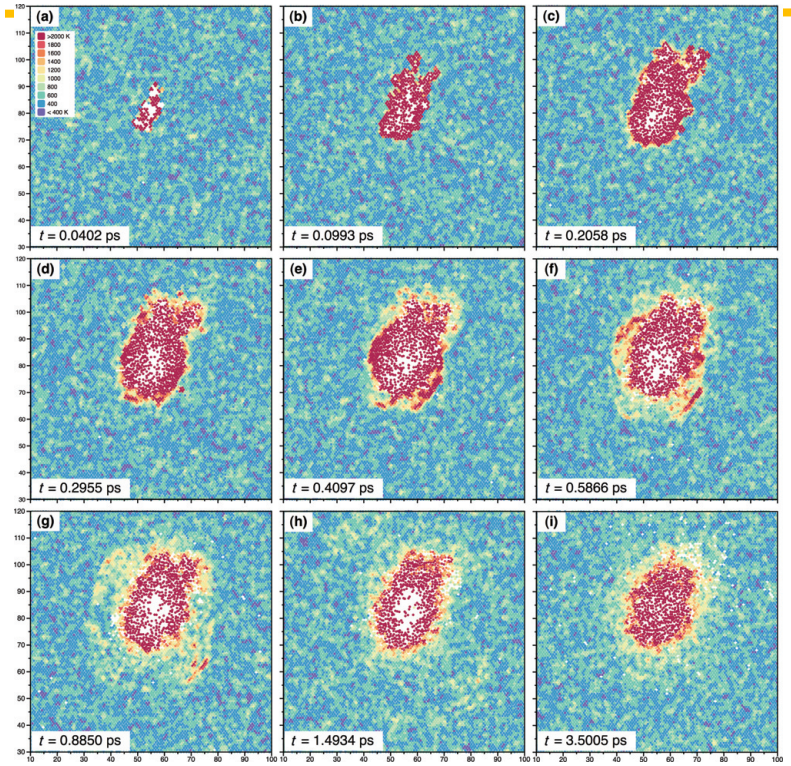
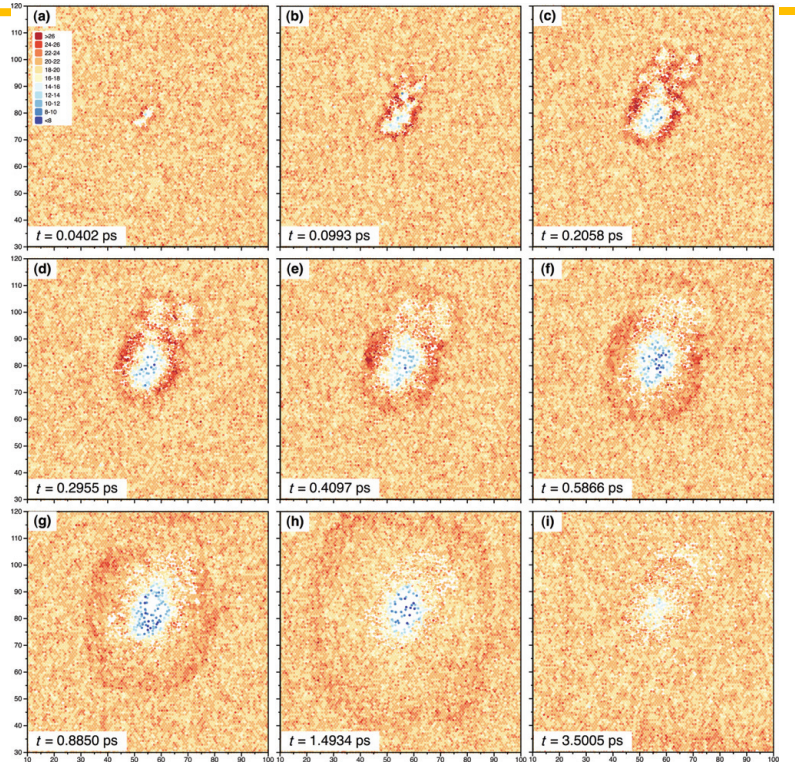
MD in Radiation Effects Studies: Formation of Interstitial Clusters

Calder, et al, Phil. Mag. **90**, 863 (2010).



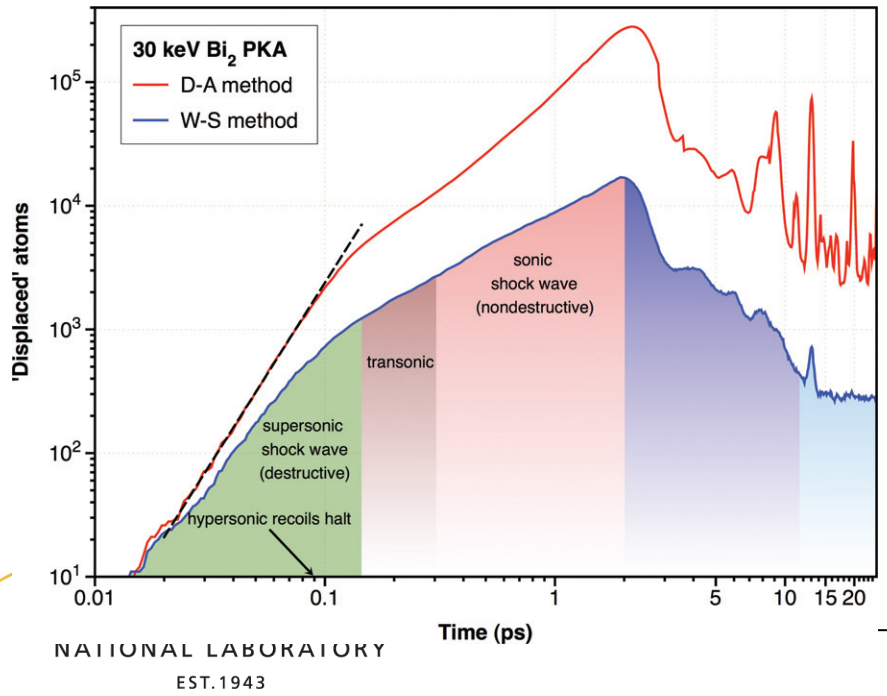


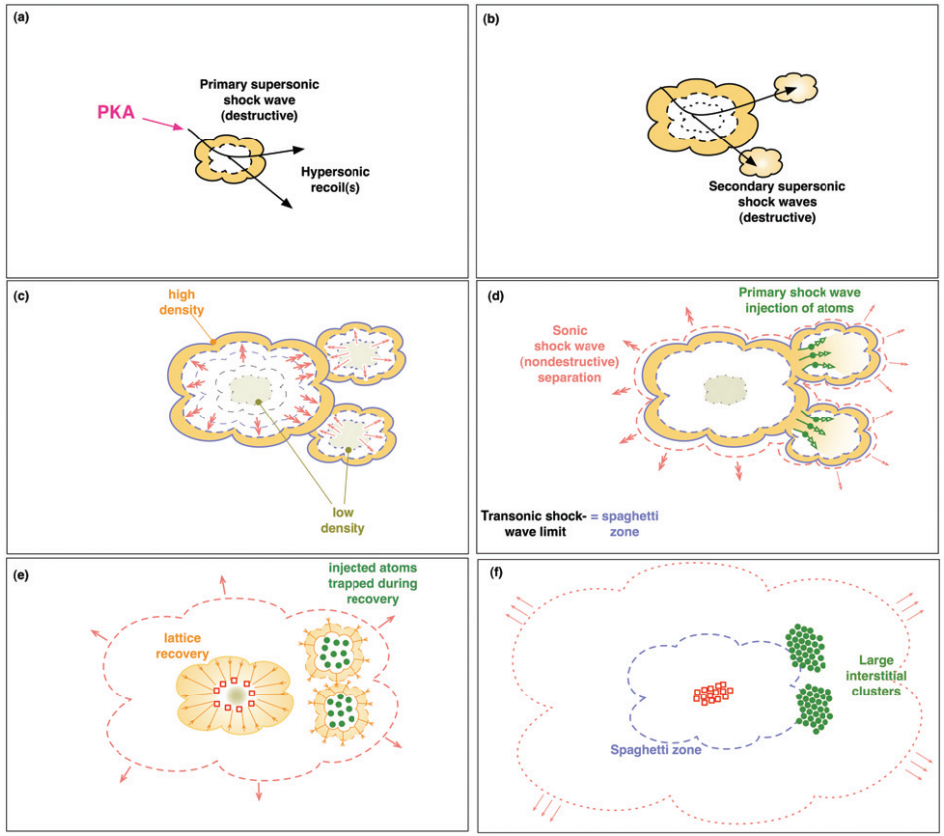
- Temperature and density evolution during a collision cascade in Fe

MD in Radiation Effects Studies: Formation of Interstitial Clusters

Calder, et al, Phil. Mag. **90**, 863 (2010).

- Via such analysis, identified several regimes of cascade evolution
- Large interstitial clusters form when interstitials from primary cascade injected into secondary cascade regions





Factors affecting accuracy and precision

- Accuracy
  - Interatomic potential
  - System size
  - Boundary conditions
  - Thermostat
- Precision
  - Integration method
  - Timestep

Active (and challenging!) area of research

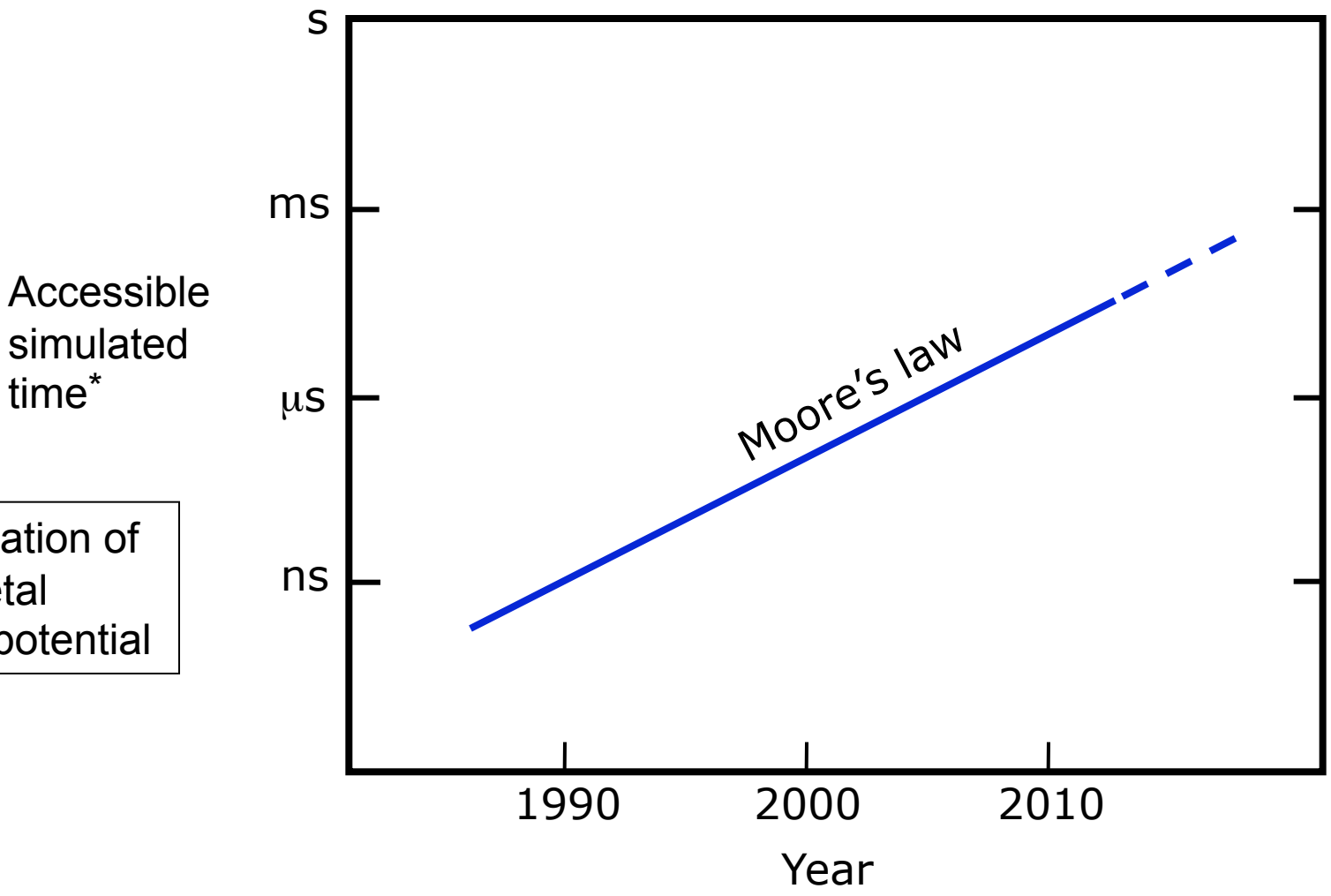
Interlude

THE TIME SCALE PROBLEM

The MD time-scale problem

- Molecular dynamics (MD) can reach nanoseconds.
- For many systems, processes we want to study often take much longer:
  - radiation damage annealing (ns, μs, ms, s, …, years)
  - vapor-deposited film growth (s)
  - creep, void growth, corrosion, catalysis,…
  - on and on …
- Often, the long-time dynamics consists of infrequent events (e.g., activated processes), for which we can define rate constants.

MD may *never* get to relevant time scales



* 1-week simulation of 1000-atom metal system, EAM potential

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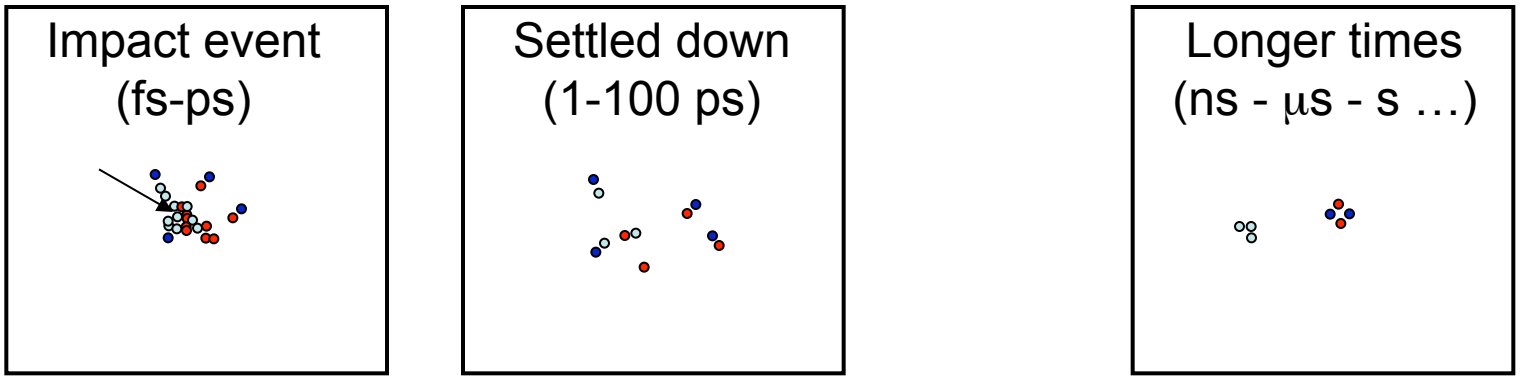
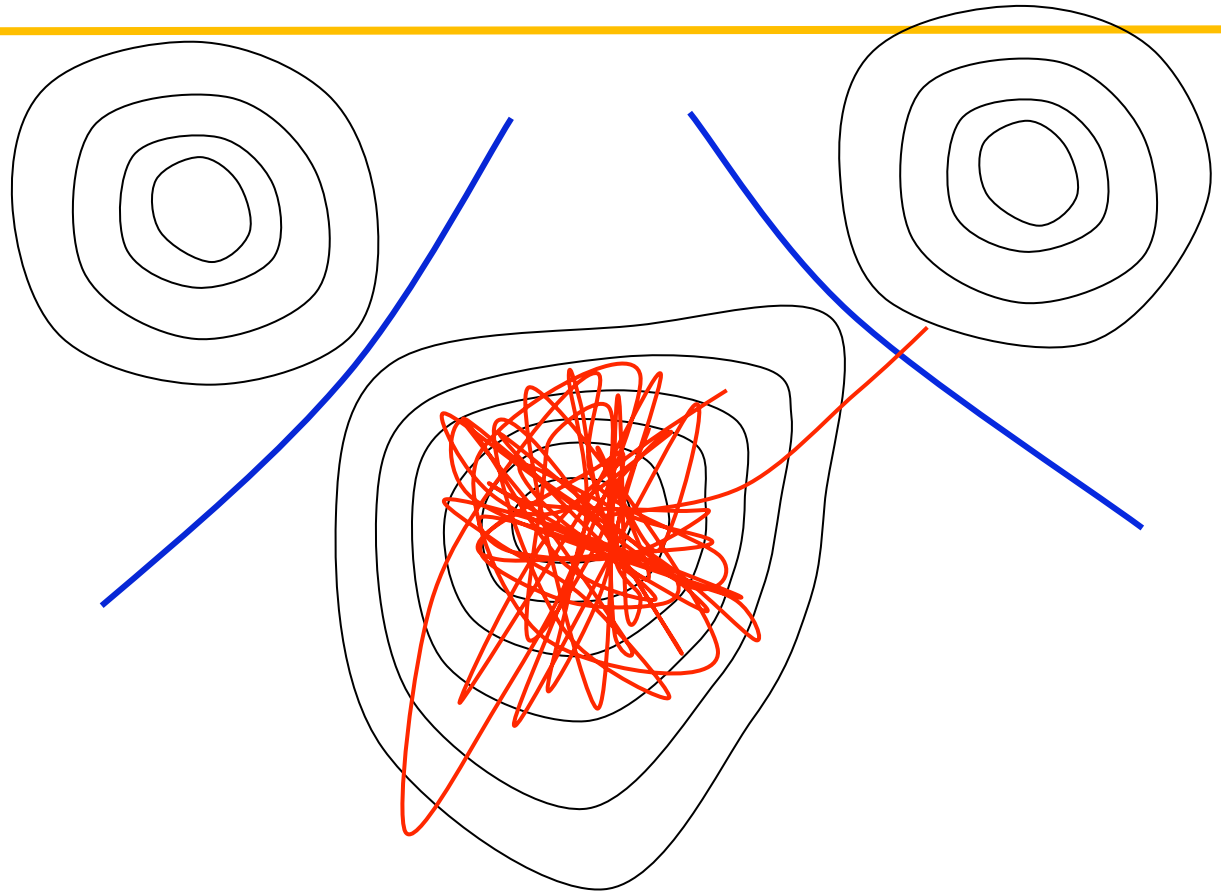
Example: Radiation Damage Annealing



Molecular dynamics (MD) ideally suited to simulate knock-on event and cascade. System settles down (becomes thermal) in a few ps.

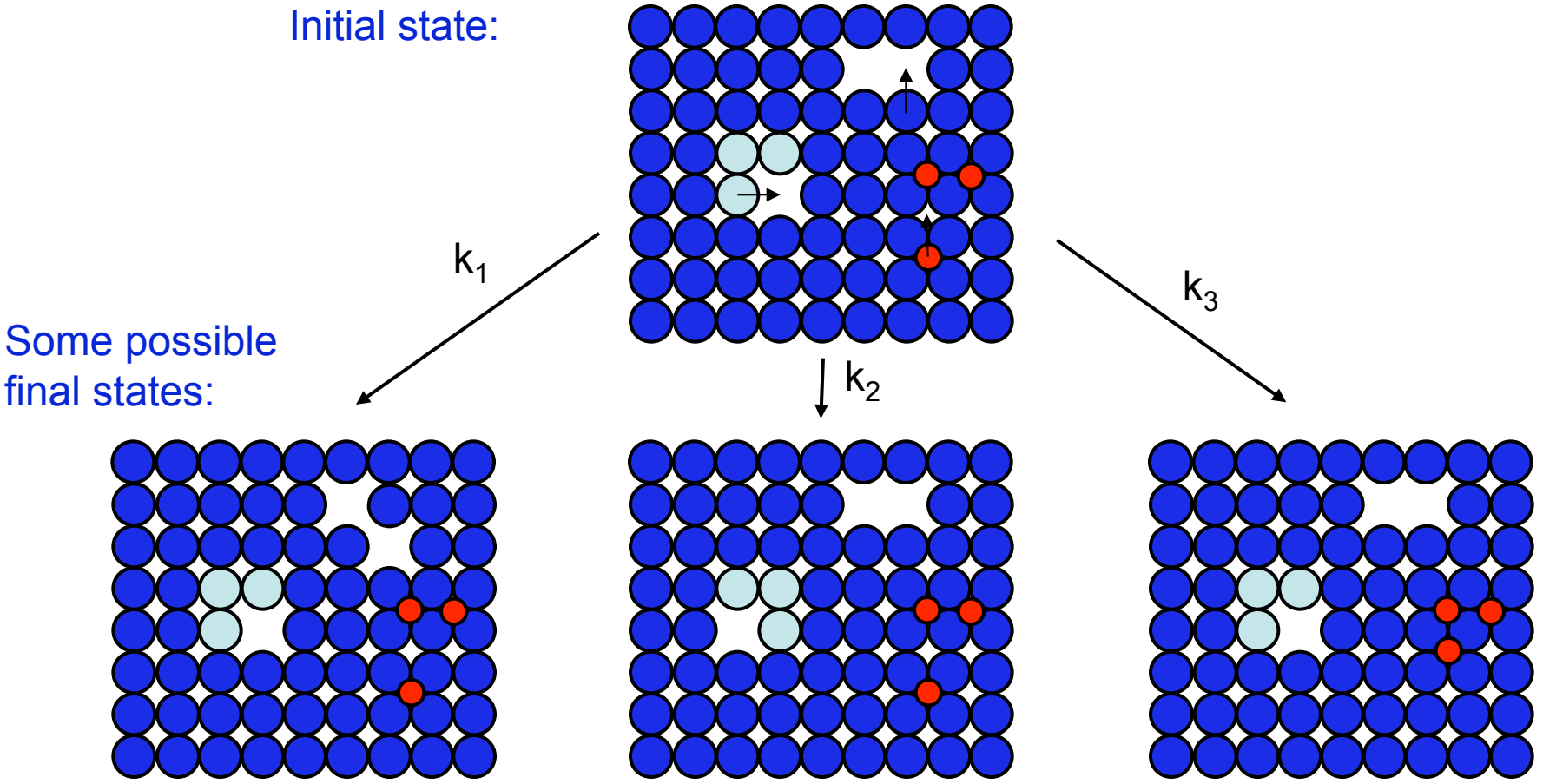
Diffusion and reorganization events can continue for much, much longer times (e.g., ms, s, …) than MD can reach.

Infrequent Event Systems



The system vibrates in a 3N-dimensional basin many times before finding an escape path. The probability that it escapes to a particular state is proportional to the rate constant (k) for escape to that state.

Examples of Escape Paths



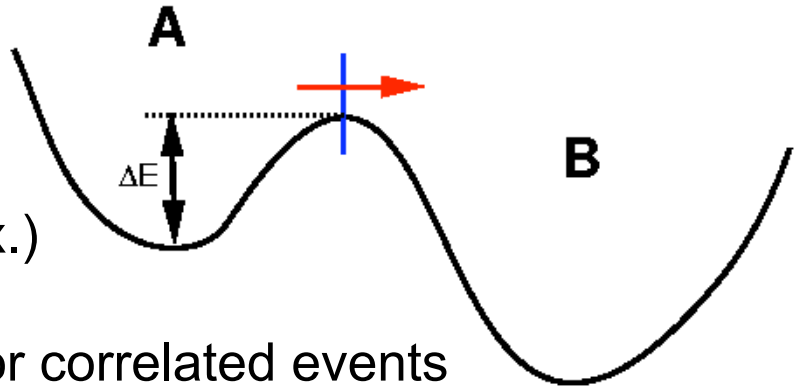
Each of these possible transitions takes the system to a new state

Transition State Theory (TST)*

TST escape rate = equilibrium flux through dividing surface at x=q

$$k_{A\to B}^{TST} = \langle \delta(x-q) \,|\, \dot{x} \,| \rangle \quad \text{(exact flux)}$$

$$k_{A\to B}^{HTST} = \upsilon_0 e^{-\Delta E / k_B T} \quad \text{(harmonic approx.)}$$

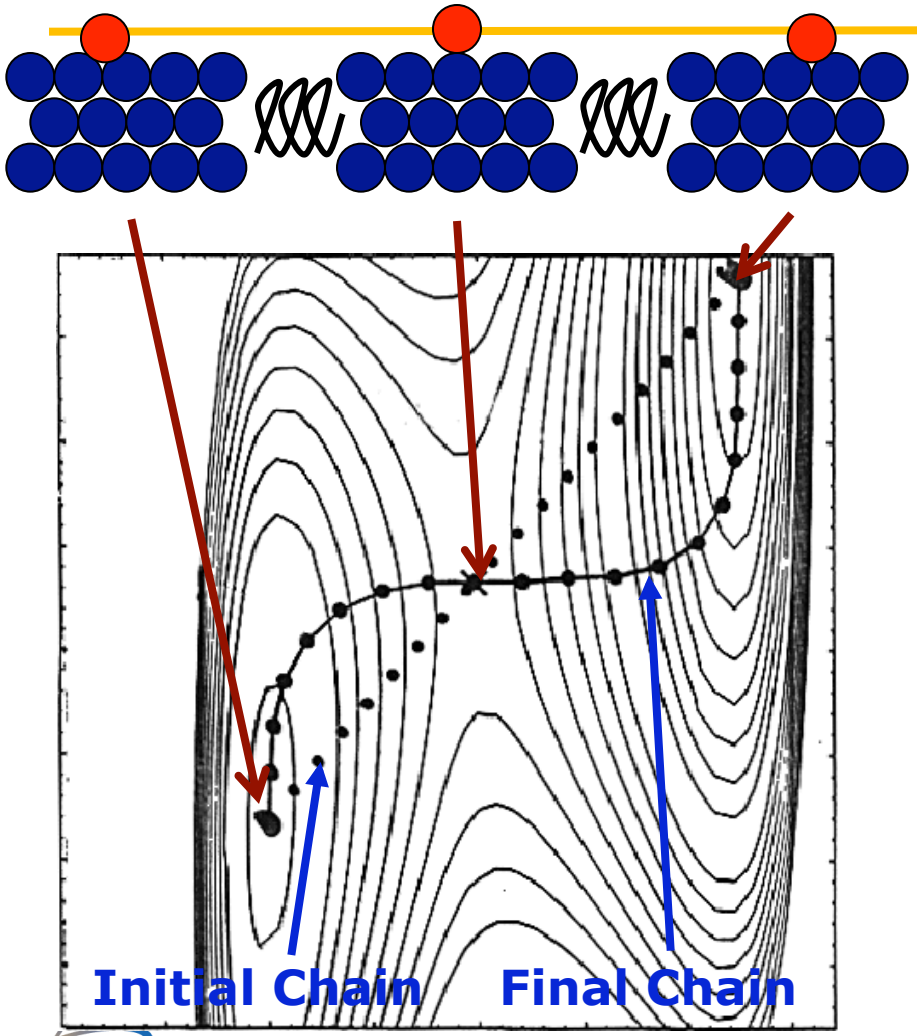


- classically exact rate if no recrossings or correlated events
- no dynamics required
- excellent approximation for materials diffusion
- traditional use of TST requires knowing dividing surface
- can also exploit TST formalism to develop methods that do not require knowing in advance where the dividing surface is

*Marcelin (1915), Wigner, Eyring, …

Nudged Elastic Band method

Mills et al, *Surf. Sci.* **324**, 305 (1995)



- To calculate $k_{A\to B}^{HTST} = \upsilon_0 e^{-\Delta E/k_B T}$ need ΔE

  →NEB

- Create multiple images of system along path from reactant to product
- Connect images with springs
- Modify forces:
  - Spring force perpendicular to path ⇒ 0
  - Real force parallel to path ⇒ 0
- Minimize entire system
- ΔE is maximum energy along this path

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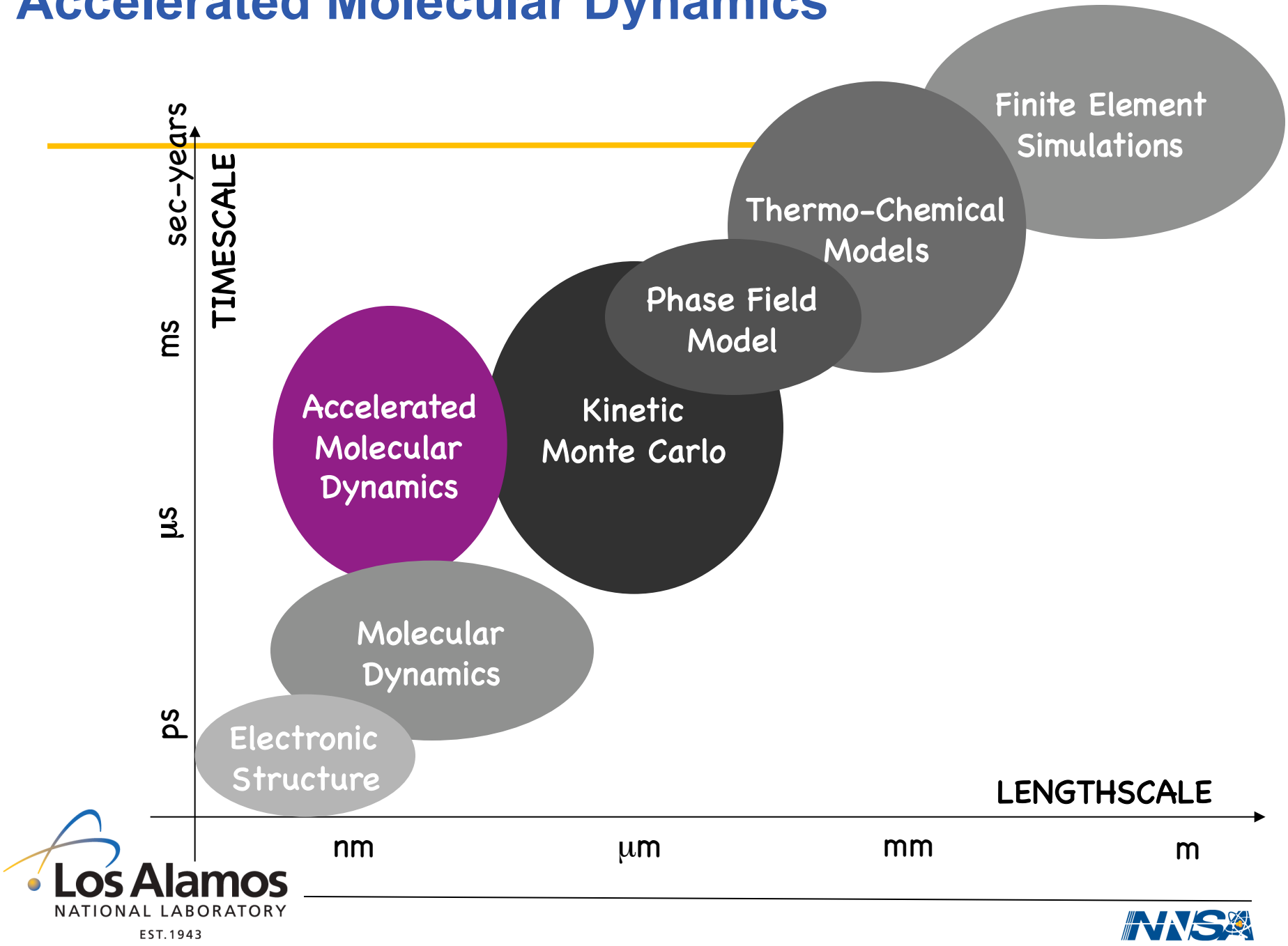
Accelerated Molecular Dynamics



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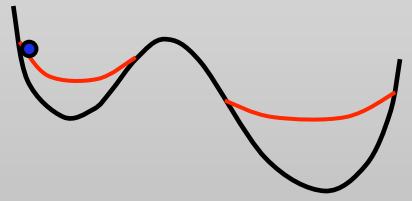
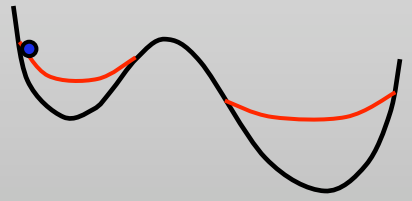
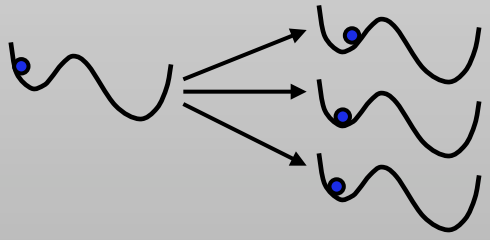
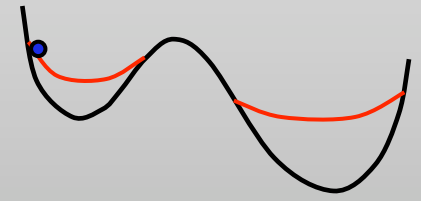
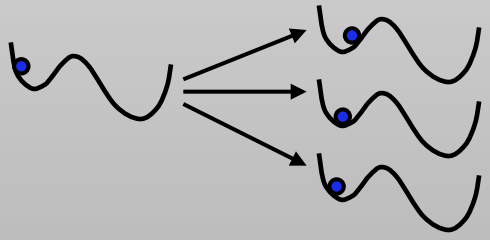
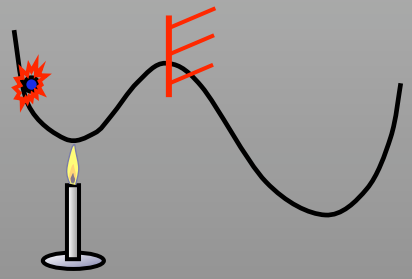
Accelerated Molecular Dynamics Methods

Hyperdynamics		Increase rate by reducing effective barriers	*AFV, J. Chem. Phys., 1997*

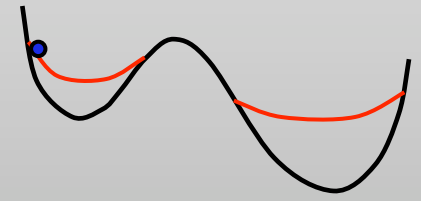
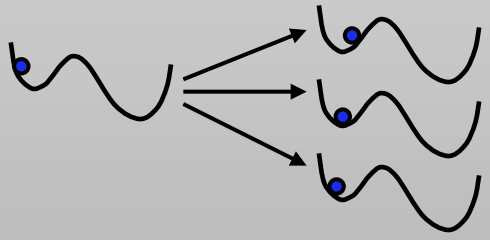
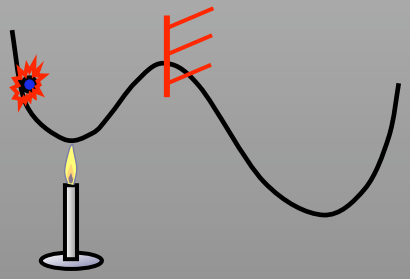
Accelerated Molecular Dynamics Methods

Hyperdynamics		Increase rate by reducing effective barriers	*AFV, J. Chem. Phys., 1997*
Parallel Replica Dynamics		Explore basin with many processors M	*AFV, Phys. Rev. B, 1998*

Accelerated Molecular Dynamics Methods

Hyperdynamics		Increase rate by reducing effective barriers	*AFV, J. Chem. Phys., 1997*
Parallel Replica Dynamics		Explore basin with many processors M	*AFV, Phys. Rev. B, 1998*
Temperature Accelerated Dynamics		Increase rate by raising temperature	*M.R. Sorensen and AFV, J. Chem. Phys., 2000*

Accelerated Molecular Dynamics Methods

Hyperdynamics		Increase rate by reducing effective barriers	*AFV, J. Chem. Phys., 1997*
Parallel Replica Dynamics		Explore basin with many processors M	*AFV, Phys. Rev. B, 1998*
Temperature Accelerated Dynamics		Increase rate by raising temperature	*M.R. Sorensen and AFV, J. Chem. Phys., 2000*

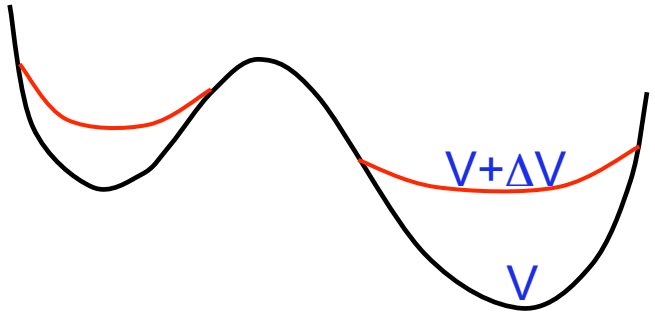
Common Themes: - reduce waiting time for a transition to order of picoseconds;
- let trajectory find transitions "naturally"

Introduction to Hyperdynamics

Voter, *JCP* **106**, 4665 (1997)

- Builds on umbrella-sampling techniques (e.g., Valleau 1970's); takes it into the time domain
- Assumptions:
  - infrequent events
  - transition state theory (no recrossings)
- Procedure:
  - design bias potential ΔV
    - zero at dividing surfaces
    - causes no recrossings
  - run thermostatted trajectory on the biased surface ($V+\Delta V$)
  - accumulate hypertime as

$$t_{hyper} = \Sigma \Delta t_{MD} \exp[\Delta V(R(t))/k_B T]$$

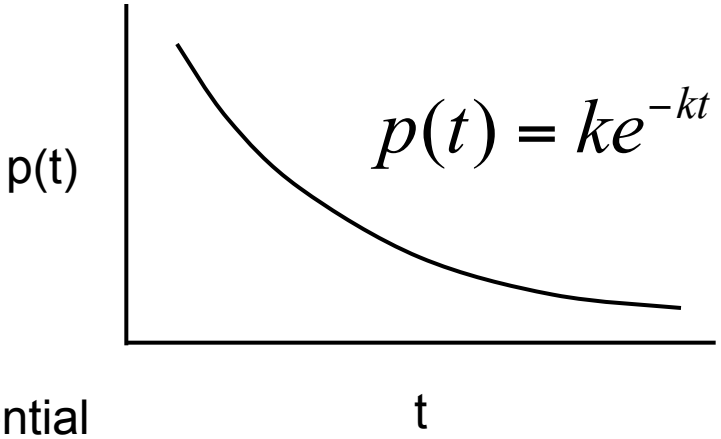


- Result:
  - state-to-state sequence correct (because relative rates are preserved)
  - time converges on correct value in long-time limit (vanishing relative error)

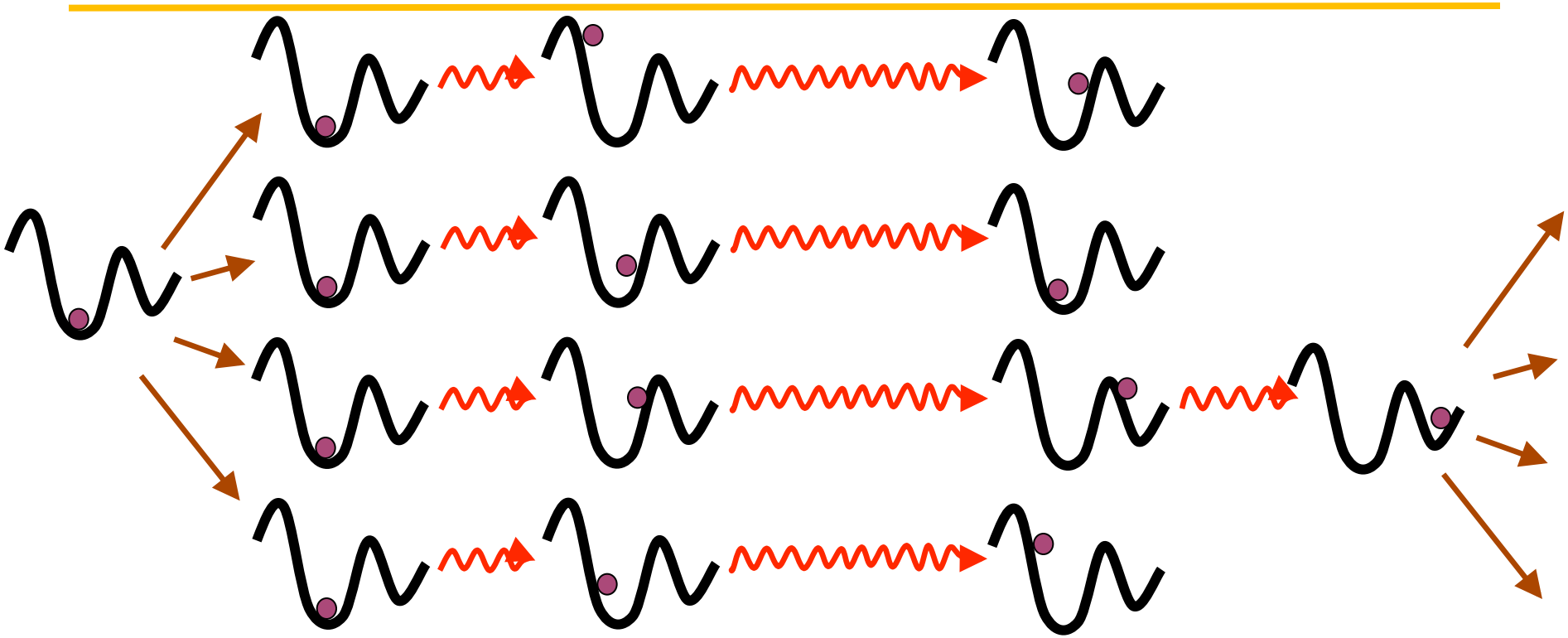
Introduction to Parallel-Replica Dynamics

Voter, *PRB* **57**, R13985 (1998)

- Offers parallel speed-up in simulation time
  - Not as “glamorous” as other methods which offer exponential speed-up on a single processor
- However, parallel-replica can be applied to systems not suited to the other methods
  - Rough potentials
  - Floppy systems with fast transitions
  - Driven systems
- Assumptions:
  - infrequent events
  - transitions can be detected
  - correlation time known
  - distribution of first-escape times is exponential

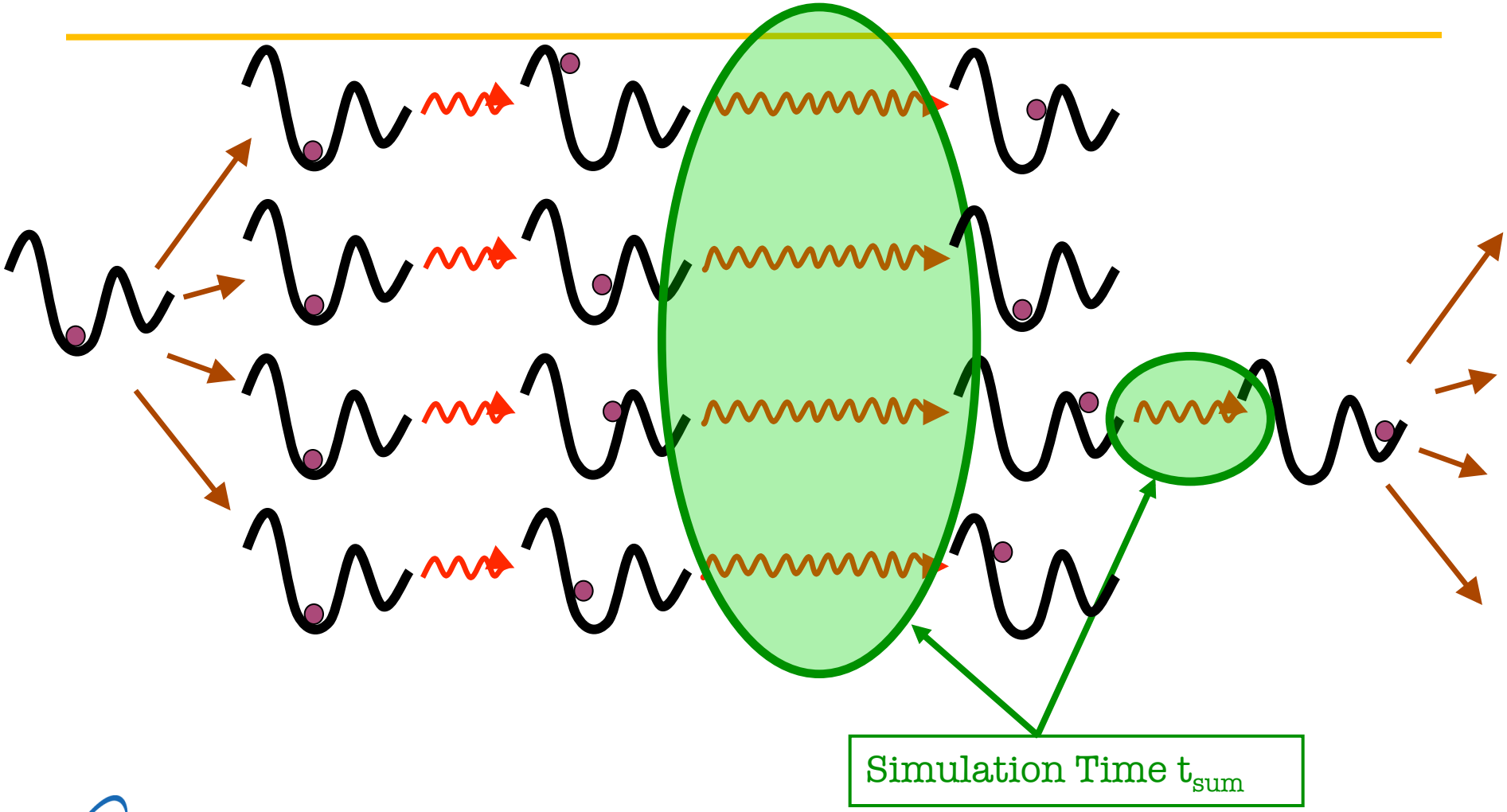


Parallel-Replica Algorithm

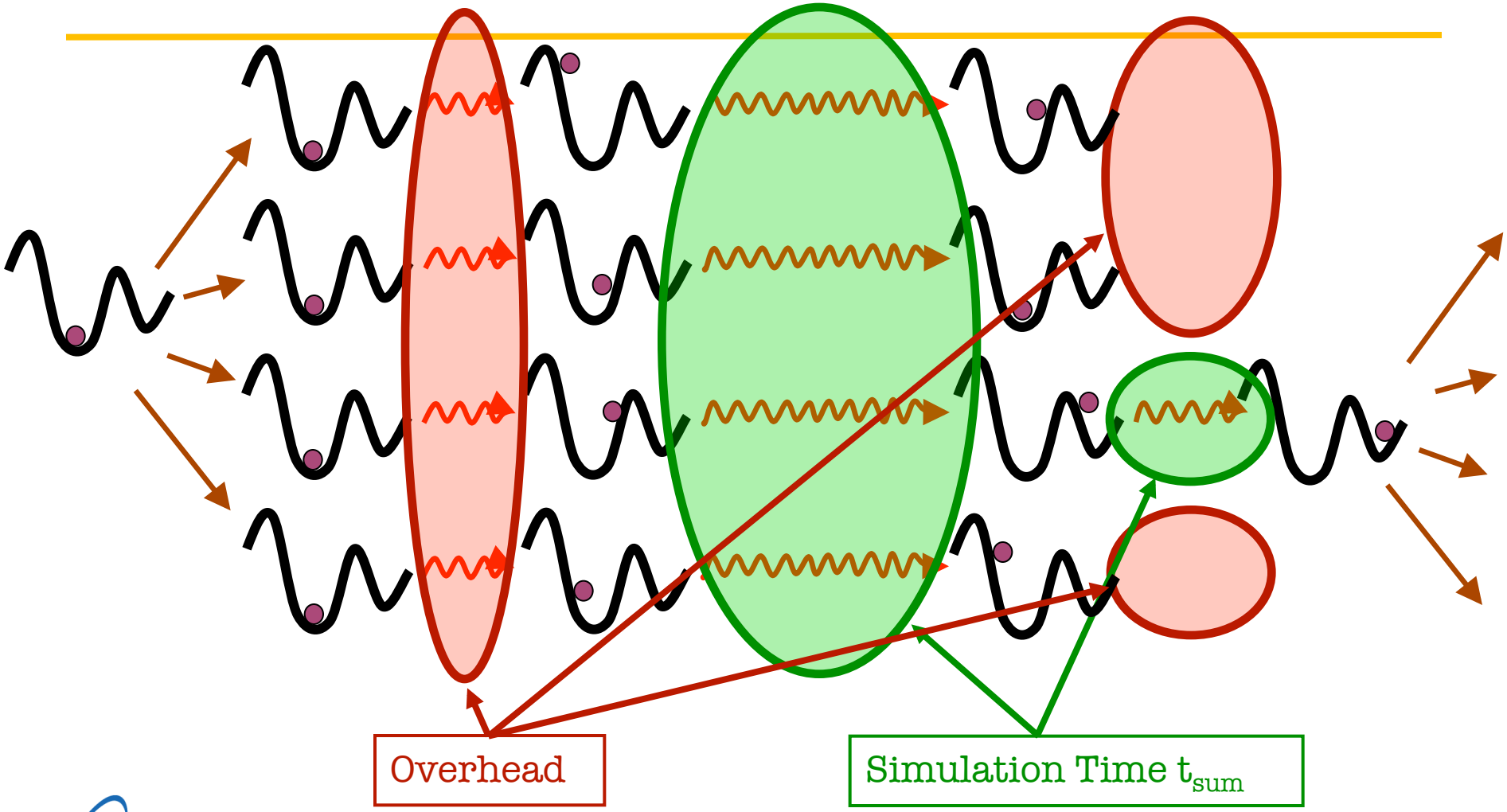


➔ Exact Longtime Dynamics

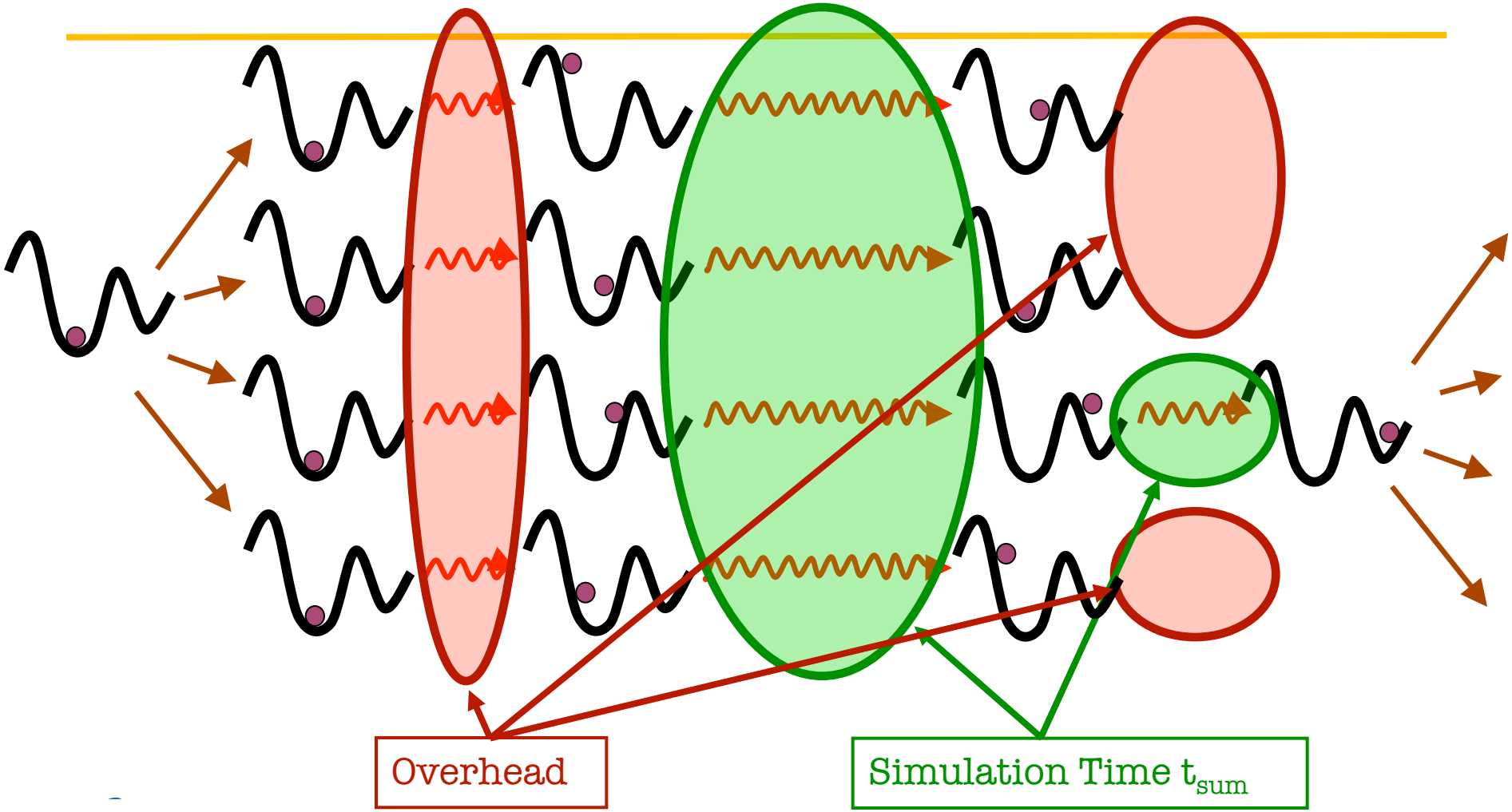
Parallel-Replica Algorithm



Parallel-Replica Algorithm



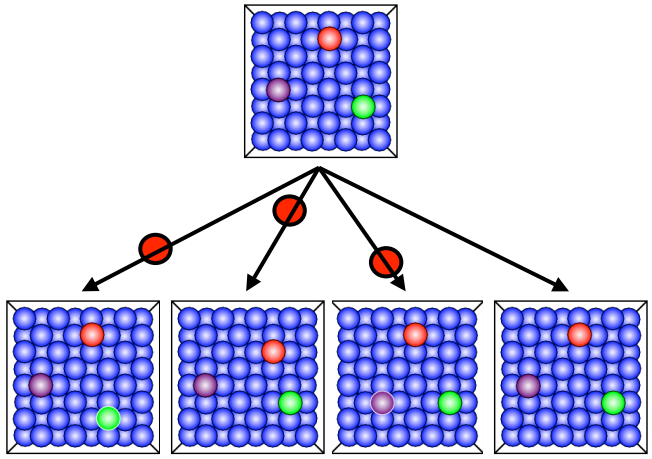
Parallel-Replica Algorithm



Good parallel efficiency if $t_{rxn} / M >> \tau_{dephase} + \tau_{corr}$

Comparison of Parallel Algorithms

Standard MD



M simulations of
size N for time t

● = event

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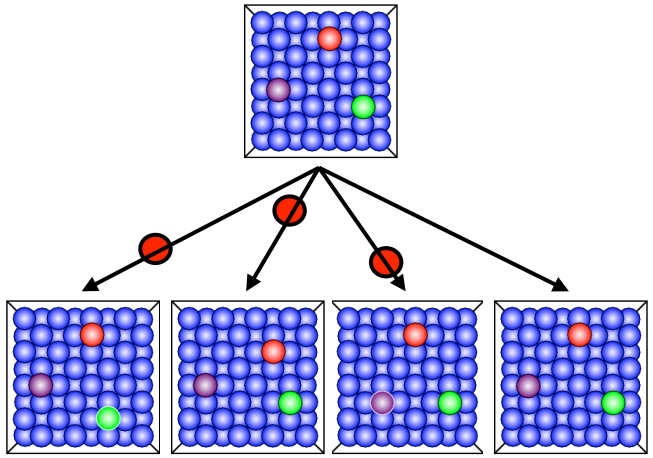
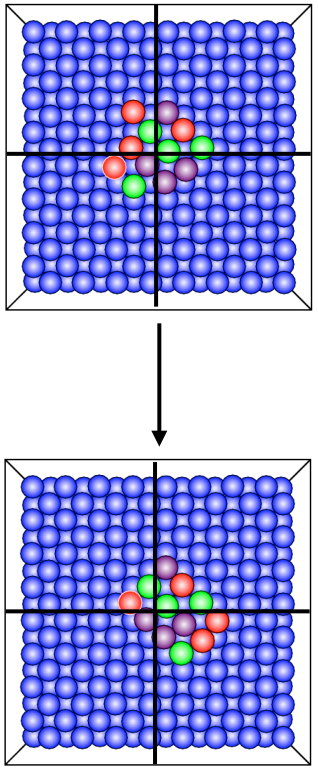
Comparison of Parallel Algorithms

Standard MD



M simulations of
size N for time t

Spatial Parallelization

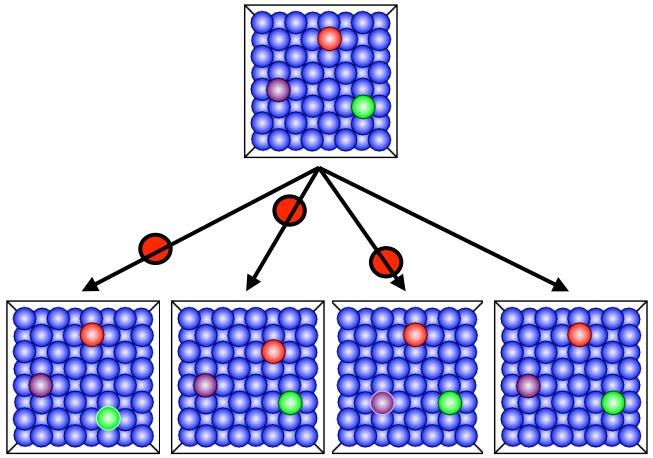


1 simulation of size
MN for time t

= event

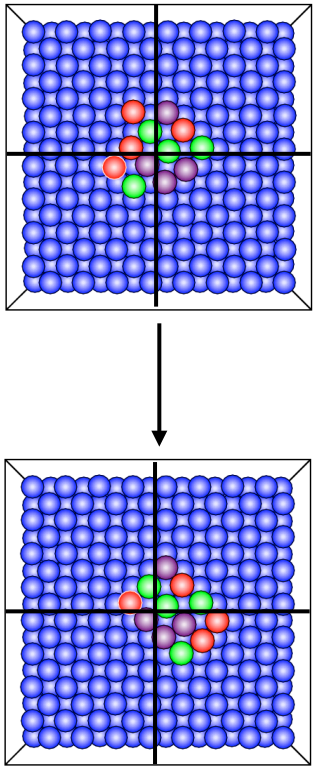
Comparison of Parallel Algorithms

Standard MD



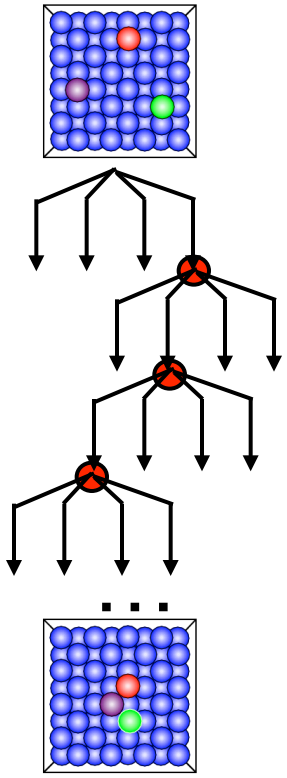
M simulations of
size N for time t

Spatial Parallelization



1 simulation of size
MN for time t

Parallel-Replica

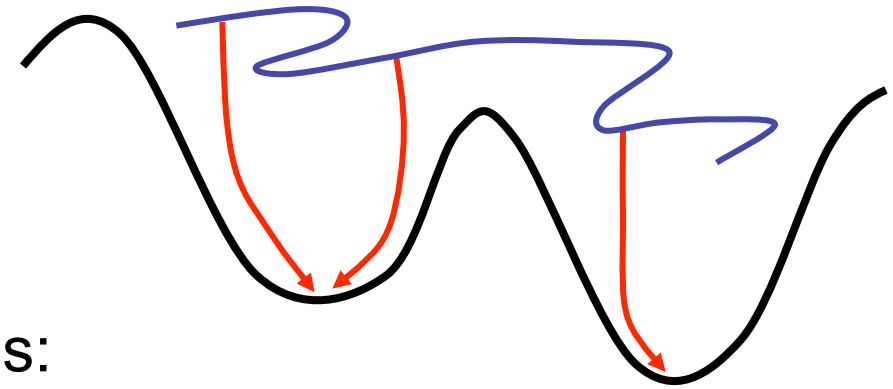


1 simulation of size
N for time Mt

= event

Detecting a Transition

- Best method depends on the system
- Simple method for EAM metal systems:
  - periodically perform minimization
  - see if geometry at basin minimum has changed



- Other Methods:
  - change in bond connectivity/length (covalent systems) (Kum, Uberuaga)
  - change in energy fluctuations (Pande)

Summary - Parallel-Replica Dynamics

- Most exact of the accelerated dynamics methods
  - no harmonic approximation
  - goes beyond TST to include correlated dynamical events
  - no assumption that barrier is energetic - can be entropic
- Easy to implement – requirements:
  - transition detection
  - good estimate of correlation time
- Very general applicability
  - any system with exponentially distributed events
- Good match to increasing availability of parallel processing power, distributed computing, etc.

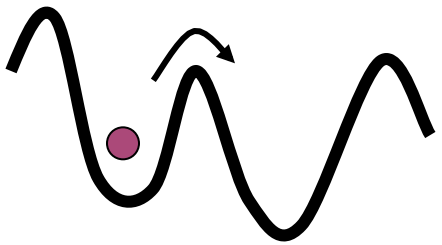
Limitations - Parallel-Replica Dynamics

- Only get parallel boost
  - If statistics are necessary such that number of samples is equal to or greater than number of processors, better to do MD
- Boost drops off when events are frequent (or become frequent because so many processors)
  - Requires “tuning” number of processors to temperature of interest
- Boost especially limited if correlation time is long
- For complex systems (e.g., proteins) even transition detection can be tricky

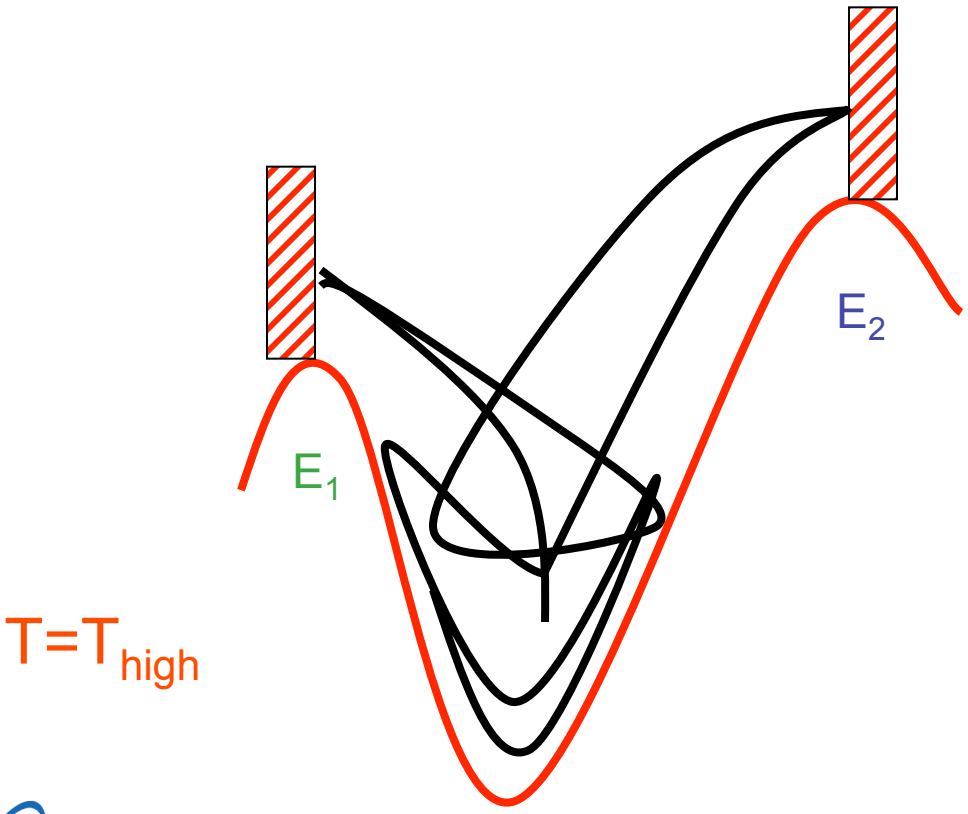
Introduction to Temperature Accelerated Dynamics

Sørensen and Voter,
JCP **112**, 9599 (2000)

- Concept:
  - System characterized by deep energy wells
  - Run basin constrained MD at high temperature
  - Extrapolate behavior to low temperature
- Approximations: $\left(k = \nu e^{-\Delta E / k_B T} \right)$
  - Harmonic Transition State Theory
  - Assumed minimum prefactor in system ν_{min}
  - Uncertainty level δ of missing the correct event
- Very powerful when barriers are high relative to temperature

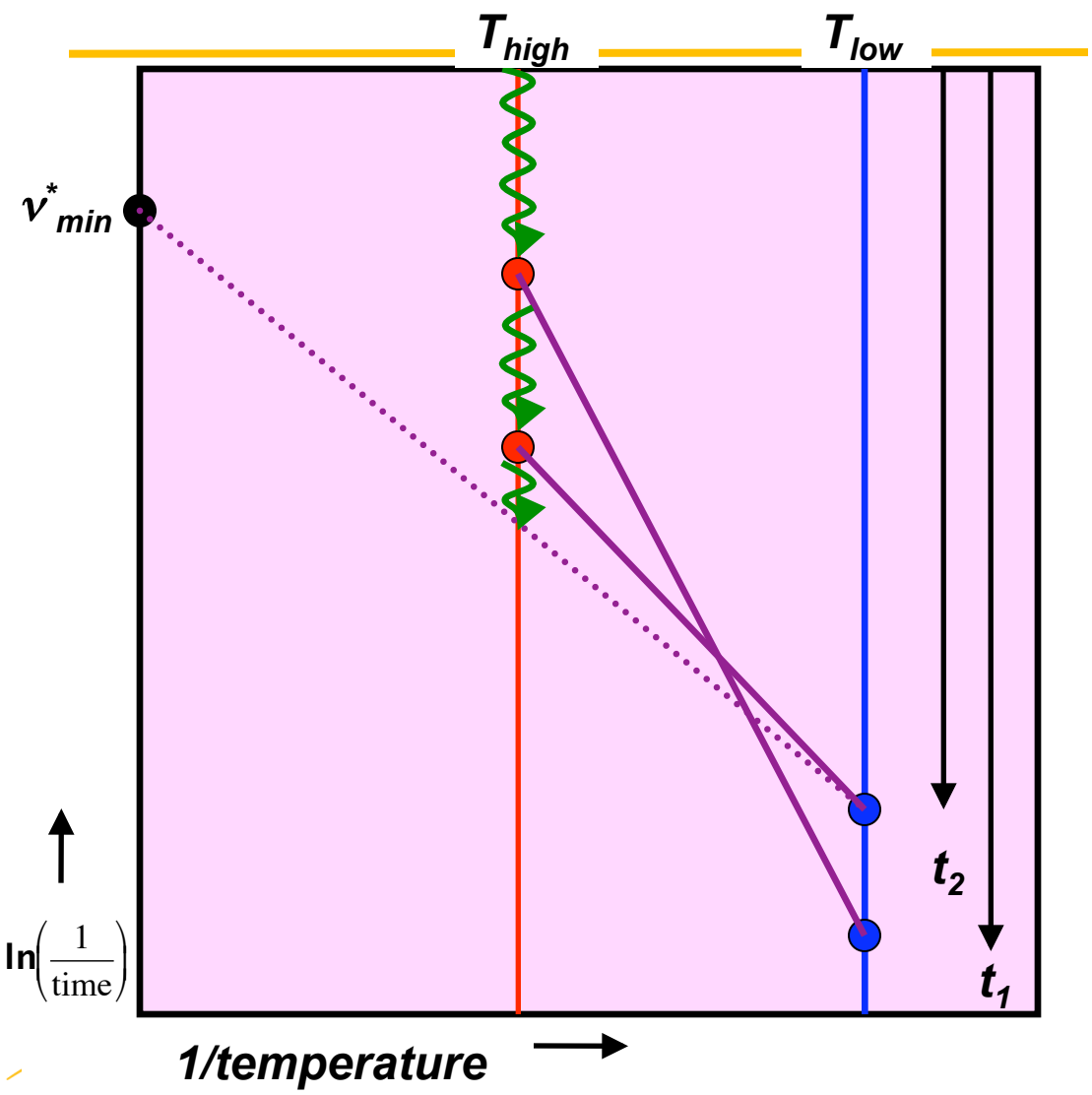


Basin Constrained MD (BCMD)



- Run dynamics at T_{high}
- When event occurs, reflect trajectory back into basin
- Continue high-T dynamics
- Reflect trajectory after any other events
- Requires:
  - Detecting transition
  - Finding energy barrier

TAD algorithm



- Do MD at T_{high} until see an event
- Find barrier, extrapolate to T_{low}, find time t_1
- Continue at T_{high} to next event
- Find barrier, extrapolate to T_{low}, find time t_2
- Continue at T_{high} until earlier event not possible (within δ)
- Accept event with earliest time (t_2)

Summary - Temperature Accelerated Dynamics

- Potentially most powerful AMD method
  - Extremely large boosts when temperature is small compared to barriers

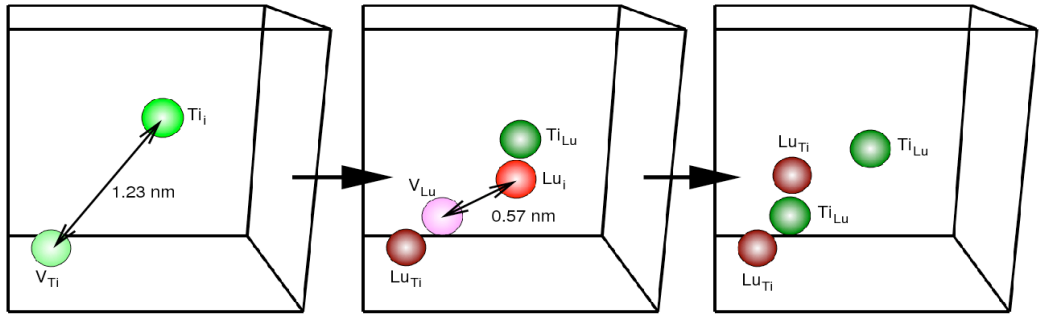
- Basic algorithm is easy to implement – requirements:
  - transition detection
  - Basin constrained MD
  - Saddle finding method

Limitations - Temperature Accelerated Dynamics

- Least exact of the accelerated MD methods
  - Assumes *harmonic* transition state theory
- For full optimization, requires many bells and whistles
  - Detect revisited states
  - Ensure events do not involve double jumps, etc
- Requires the potential to be relatively smooth for efficient saddle point calculations

Defect properties that can be simulated with AMD

- Long time kinetic evolution of defect structures
  - Unexpected mechanisms
  - Activation energies for complex processes



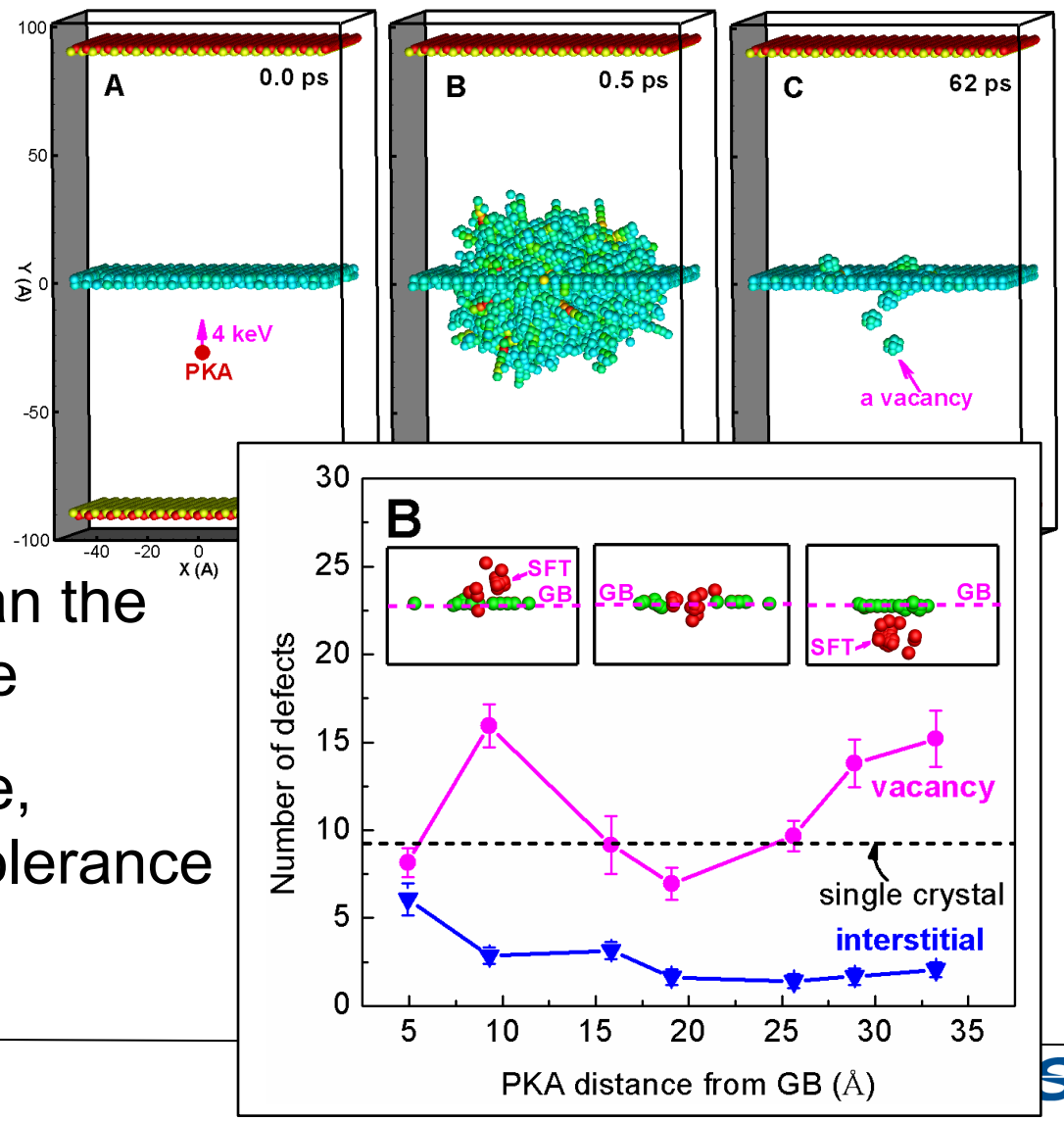
Dynamic formation of two antisite pairs from a single cation Frenkel pair in $Lu_2Ti_2O_7$ pyrochlore.

- Most properties that can be calculated with MD, but over longer time scales
- …

AMD in Radiation Effects Studies: Damage Production/Evolution near Boundaries

Bai et al, Science **327**, 1631 (2010)

- MD of PKAs near GBs in Cu
- GB absorbs interstitials
- The vacancy concentration is typically higher than the single crystal value
- At low temperature, GBs worsen rad tolerance



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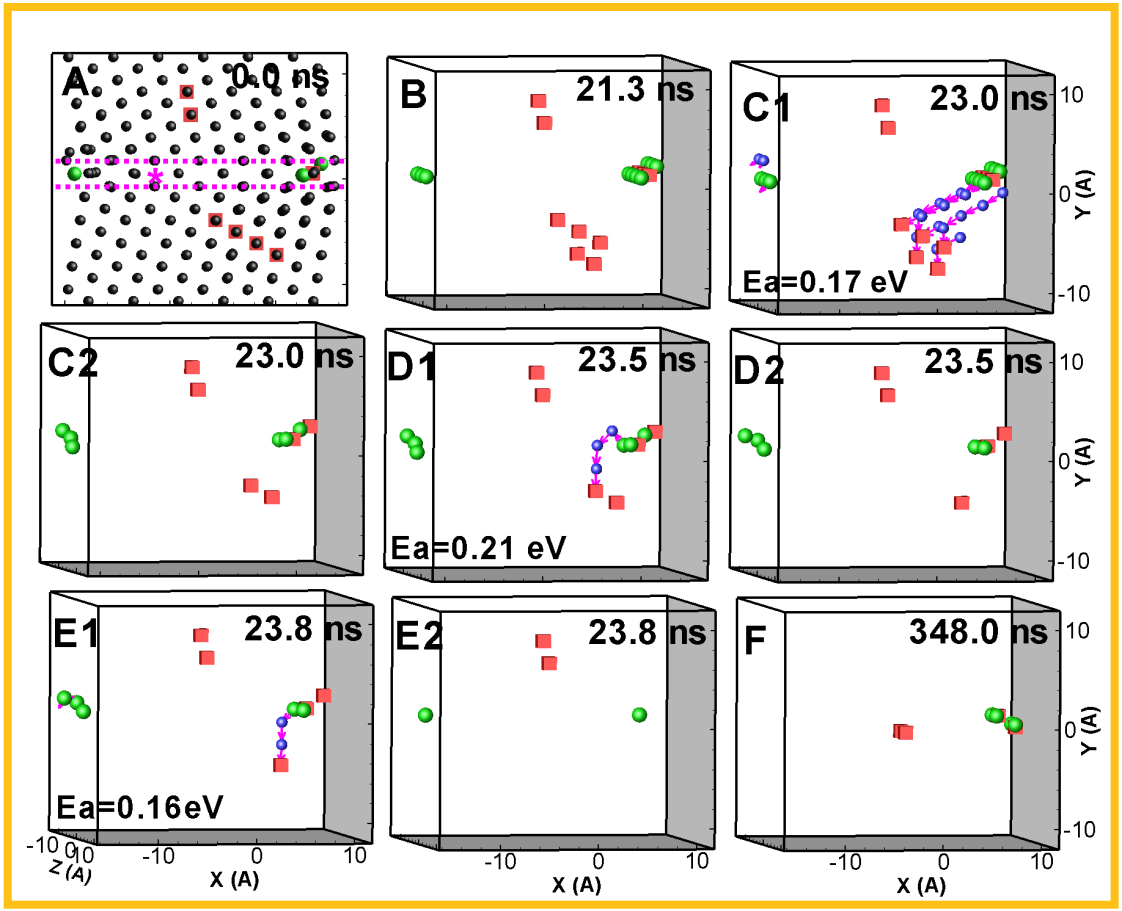
AMD in Radiation Effects Studies: Damage Production/Evolution near Boundaries

Bai et al, Science **327**, 1631 (2010)

- TAD simulation of MD damage
- Absorbed interstitials can emit to annihilate vacancies with low barriers
  - → Healing mechanism that is faster than vacancy diffusion



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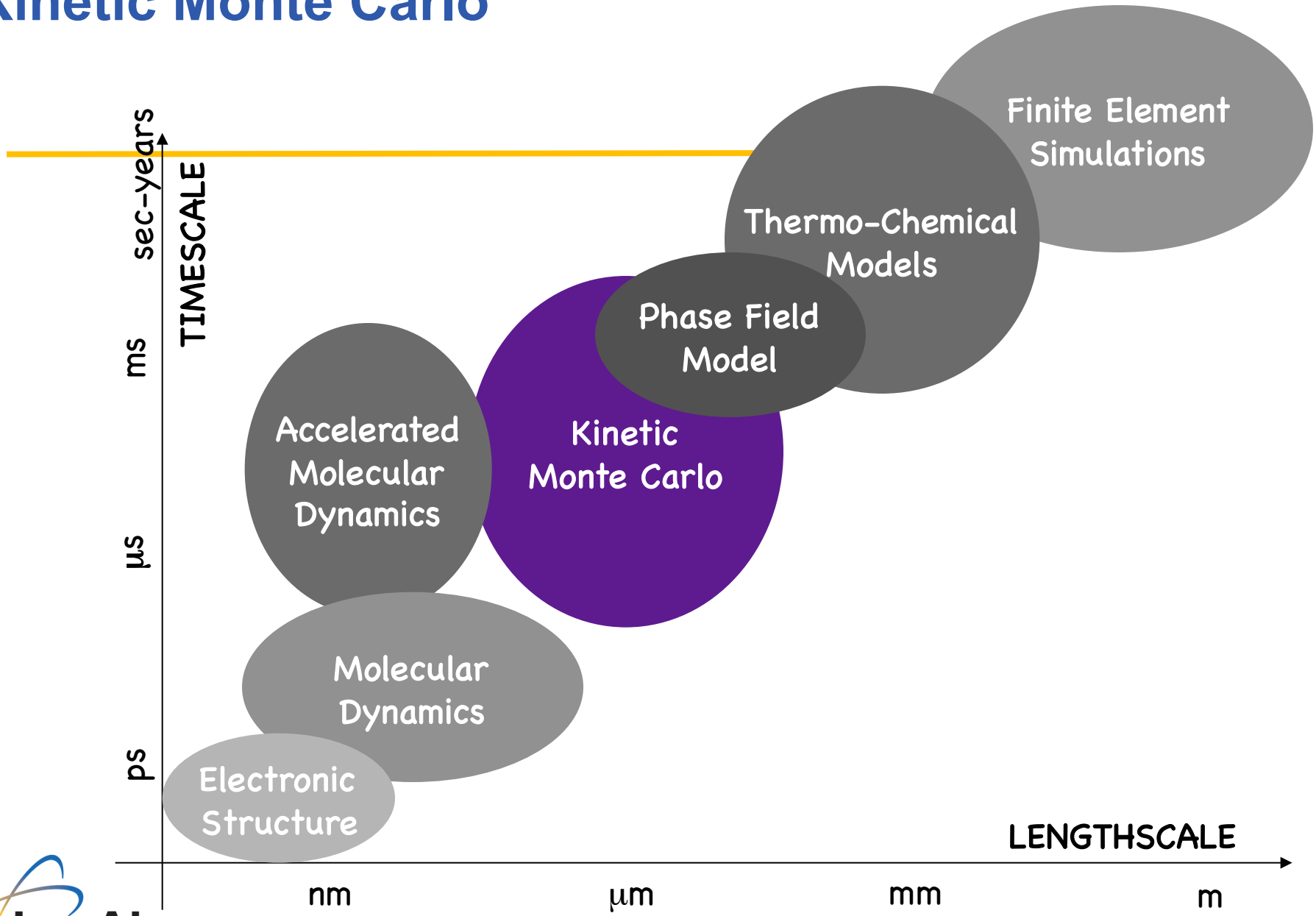
Summary

- Accelerated molecular dynamics concept:
  - Let the trajectory find an appropriate way out of state, but coax it into doing so more quickly
- Significant speedup over standard MD when barriers are high relative to temperature
- Often encounter unexpected behavior
  - Many mechanisms that would be left out of e.g. KMC if intuition alone is used
    - High mobility of interstitial clusters in MgO
    - Transformation of void to stacking fault tetrahedron in Cu
    - Interstitial emission near GBs in Cu
    - Thinning of Ag nanowires
- Ongoing challenges
  - low barriers and pesky local minima
  - cuspy potentials
  - scaling with system size

Review: Voter, Montalenti, and Germann, *Ann. Rev. Mater. Res.* **32**, 321 (2002)

Kinetic Monte Carlo



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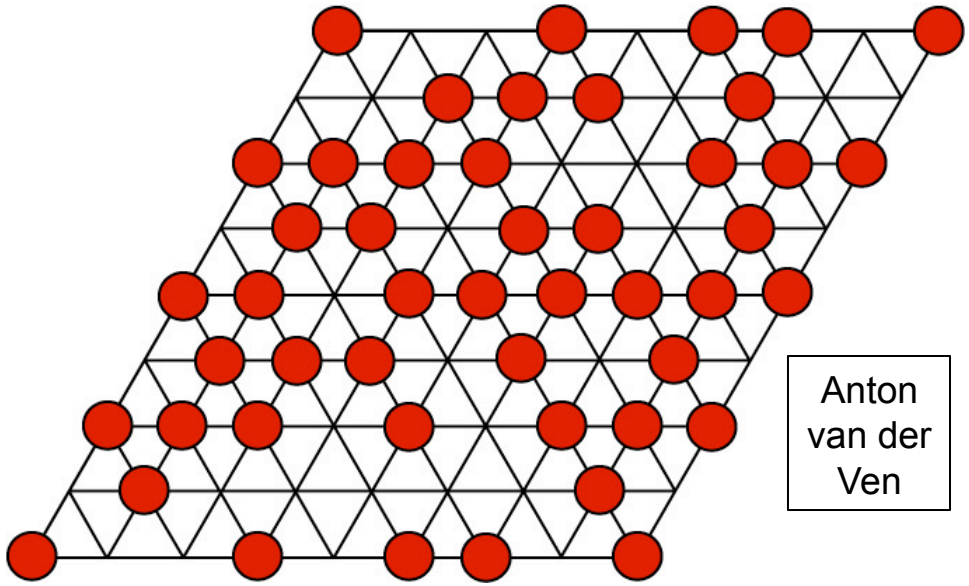
The kinetic Monte Carlo concept

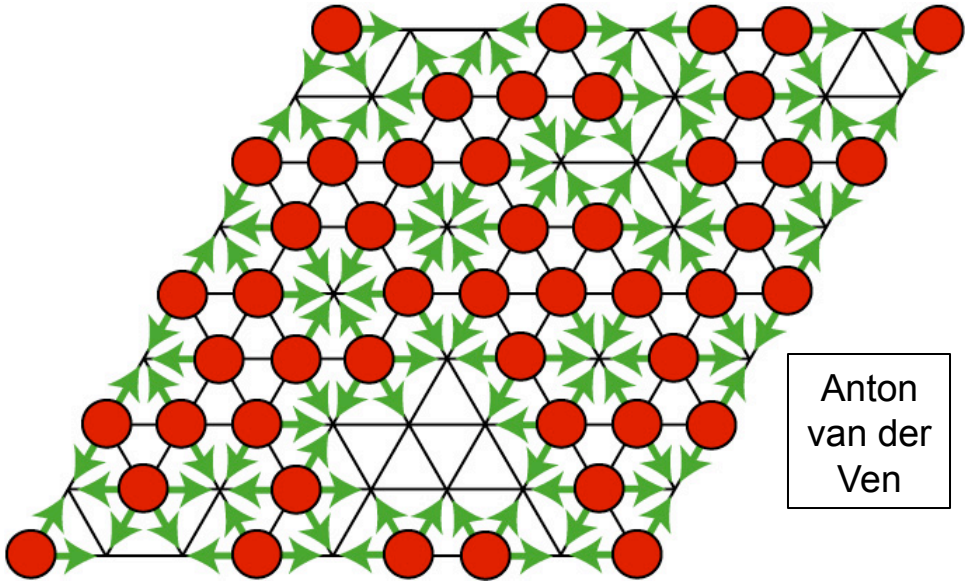
- Have an infrequent-event system in some state A



Anton van der Ven

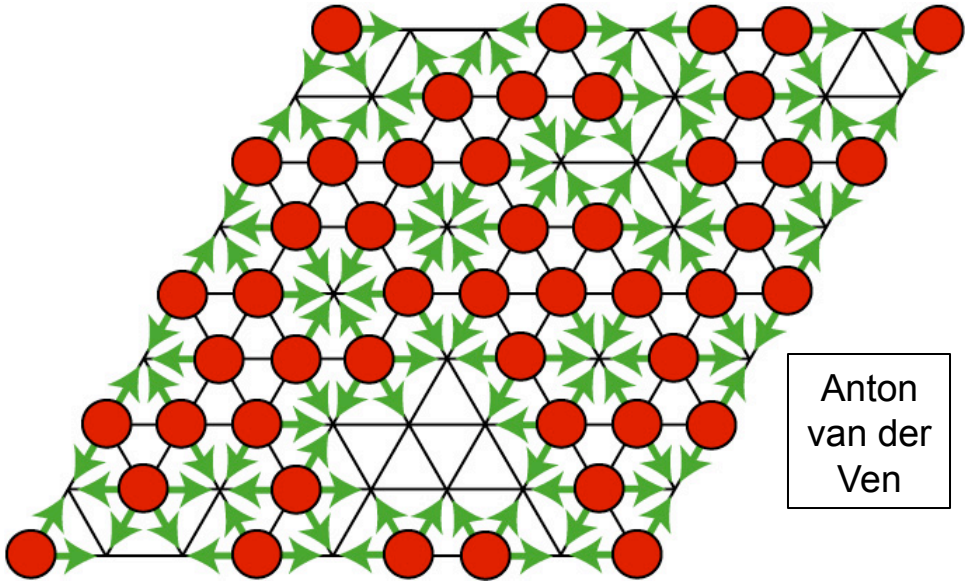
The kinetic Monte Carlo concept

- Have an infrequent-event system in some state A
- There is a set of states {X} to which the system can escape



The kinetic Monte Carlo concept

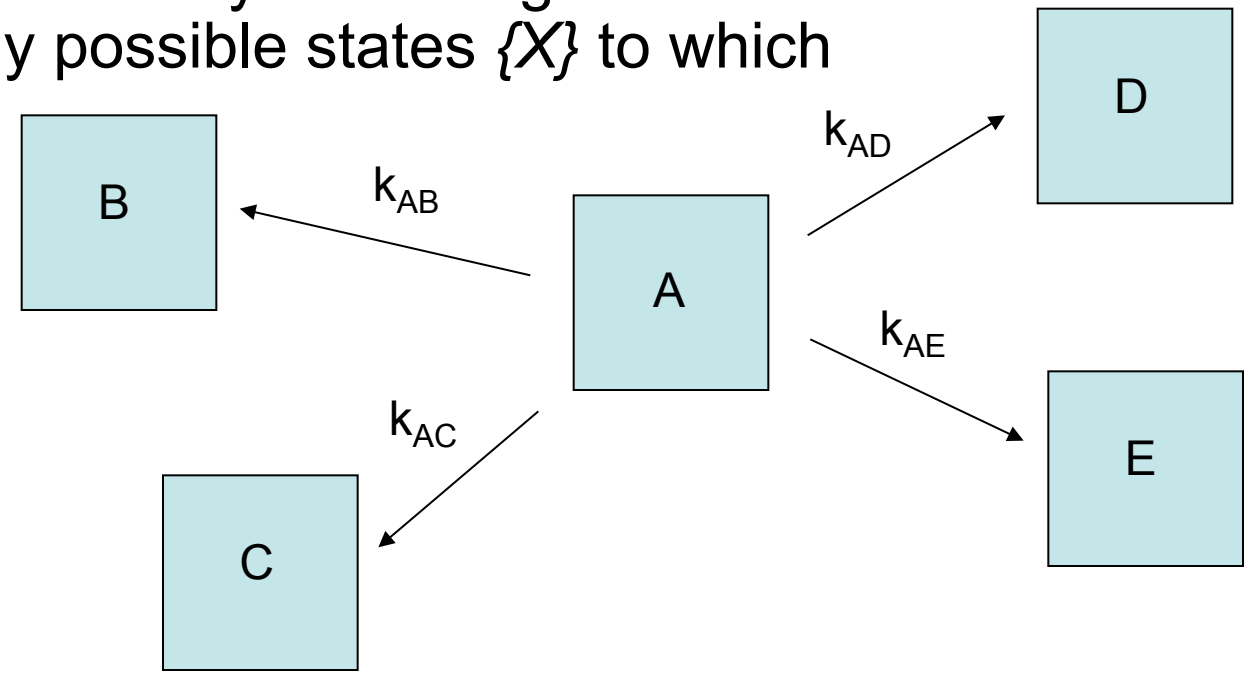
- Have an infrequent-event system in some state A
- There is a set of states {X} to which the system can escape
- If we know the rate constant (k_{AX}) for each of these paths…
- The KMC algorithm propagates the system from state A to the next state with the correct relative probability.
- Iterating this procedure propagates the system forward in time from state to state.
- For this system of states and rate constants, KMC gives exact state-to-state dynamics.



Anton van der Ven

Rate of escape for many final states

For an infrequent-event system caught in some state *A*, with many possible states *{X}* to which it can escape:

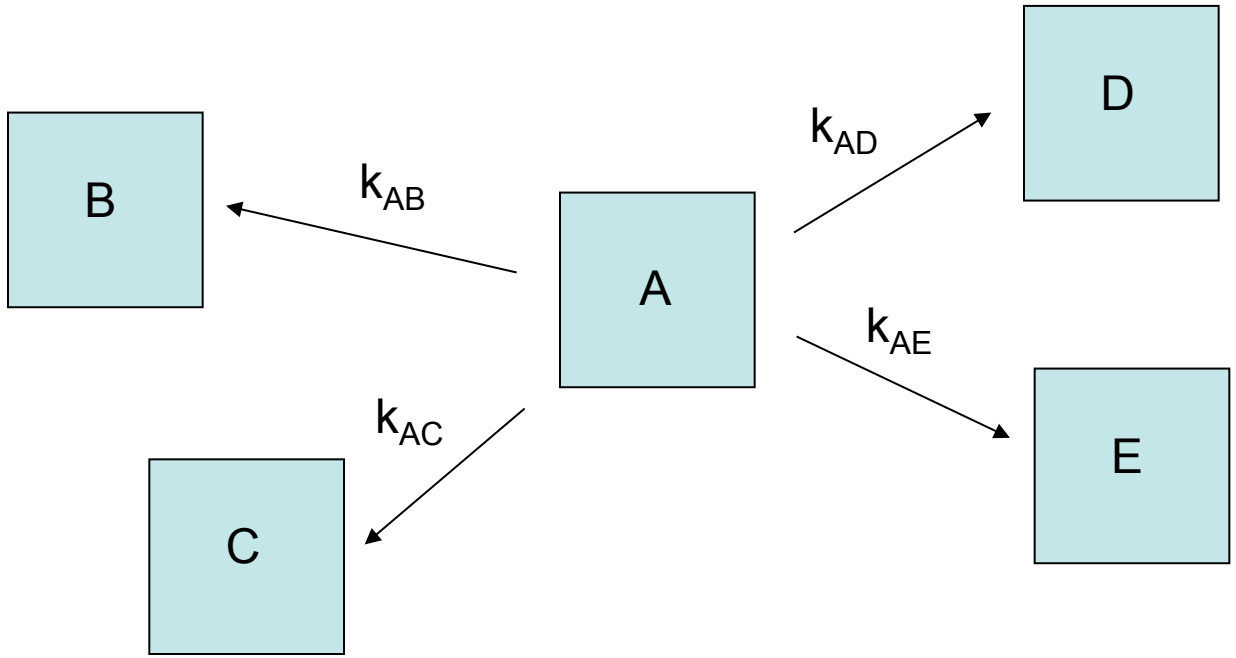


The overall first-escape time distribution is an exponential:

$$p_{TOT}(t) = k_{TOT}\exp(-k_{TOT}t), \quad k_{TOT} = \Sigma_X k_{AX}$$

The average time until an escape is $t_{ave} = 1/k_{TOT}$

Rate of escape for many final states



The overall first-escape time distribution is an exponential:

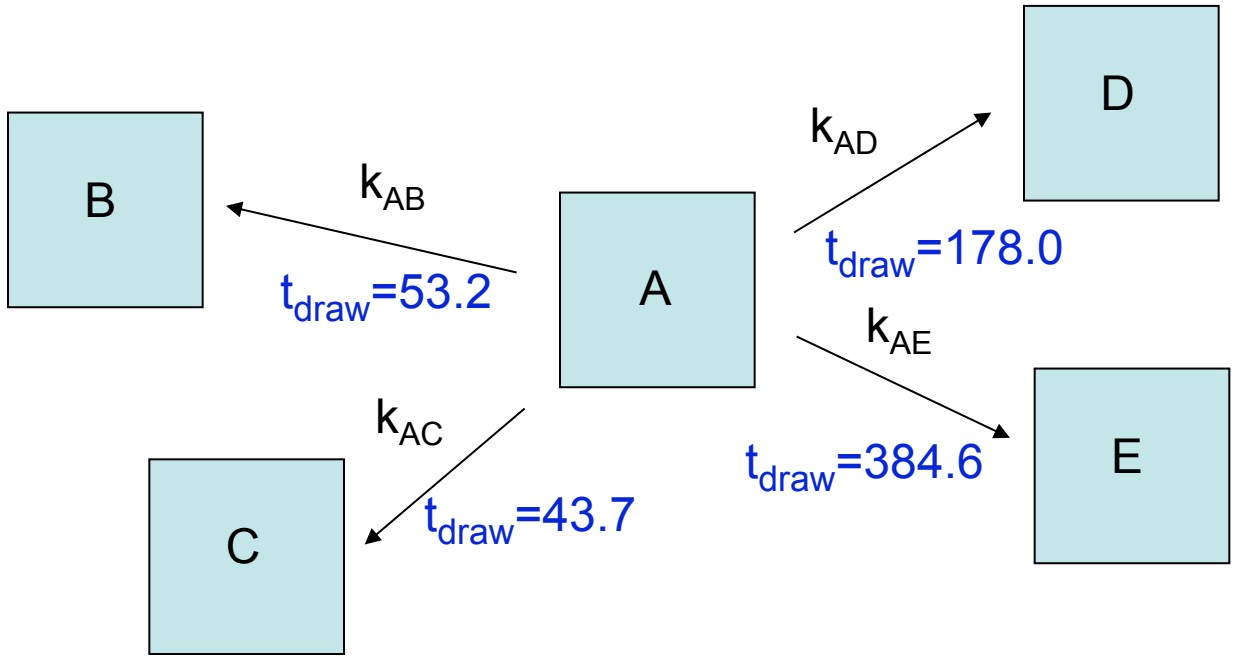
$$p_{TOT}(t) = k_{TOT}\exp(-k_{TOT}t), \qquad k_{TOT} = \Sigma_X k_{AX}$$

And each individual path's first-escape time is exponential:

$$p_{AX}(t) = k_{AX}\exp(-k_{AX}t)$$

but only ONE can happen first

Rate of escape for many final states



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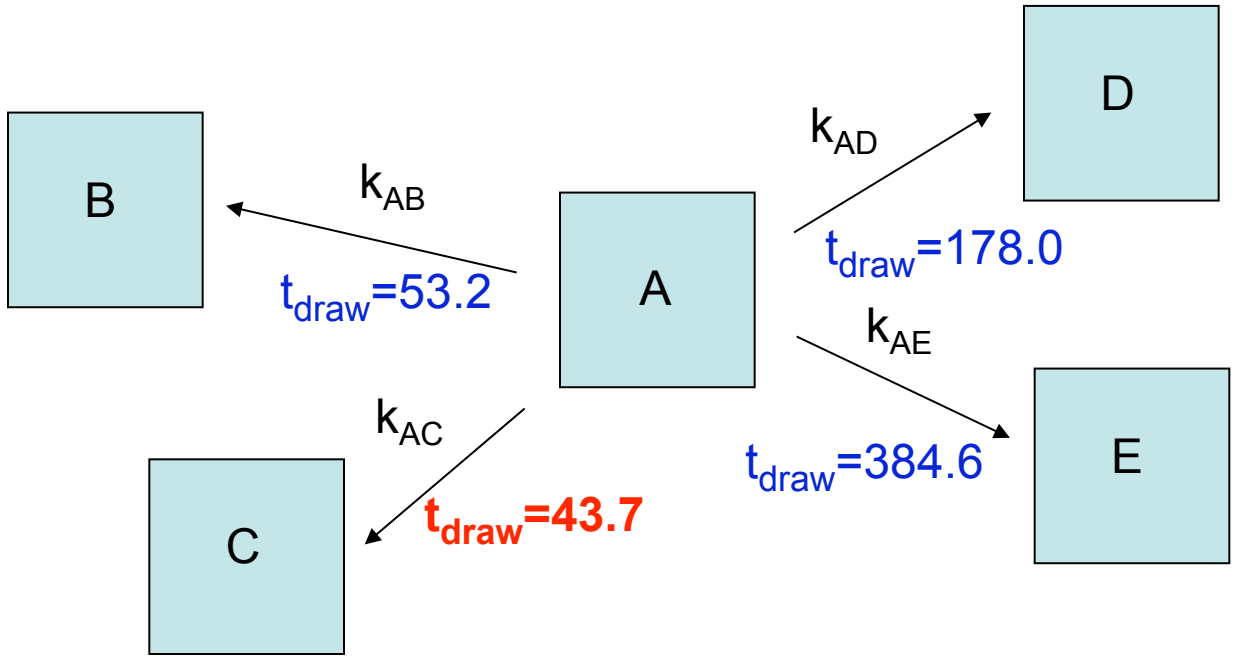
Rate of escape for many final states



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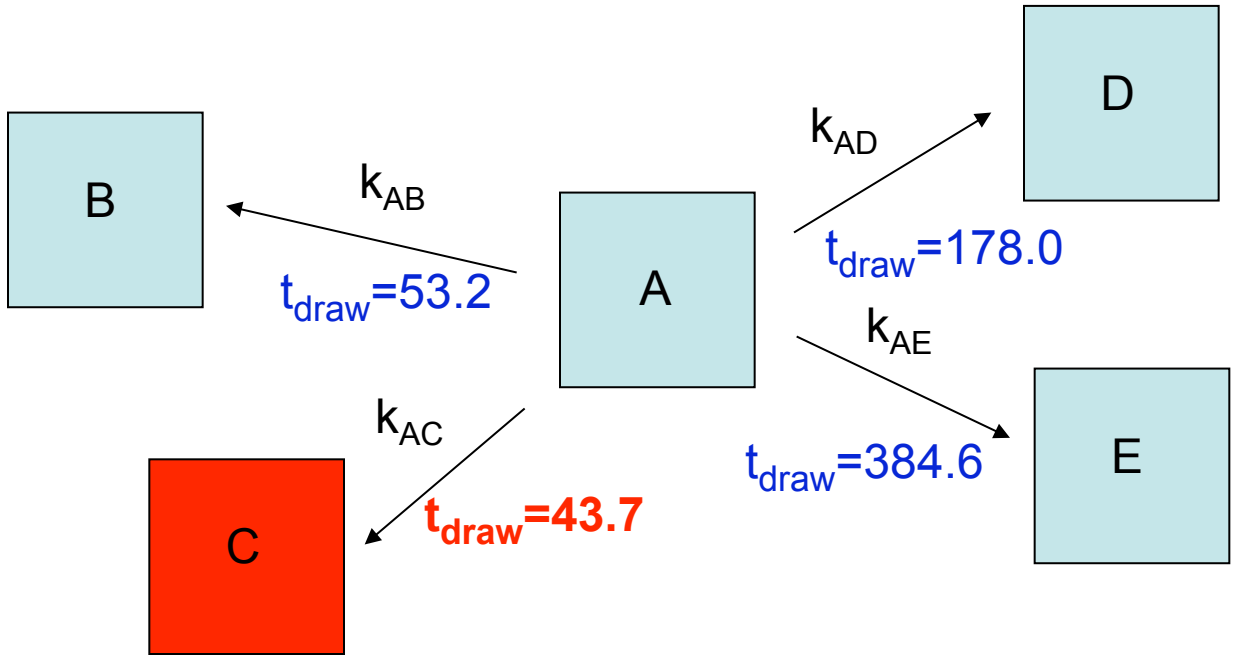
but only ONE can happen first

Rate of escape for many final states



The overall first-escape time distribution is an exponential:

$$p_{TOT}(t) = k_{TOT}\exp(-k_{TOT}t), \qquad k_{TOT} = \Sigma_X k_{AX}$$

And each individual path's first-escape time is exponential:

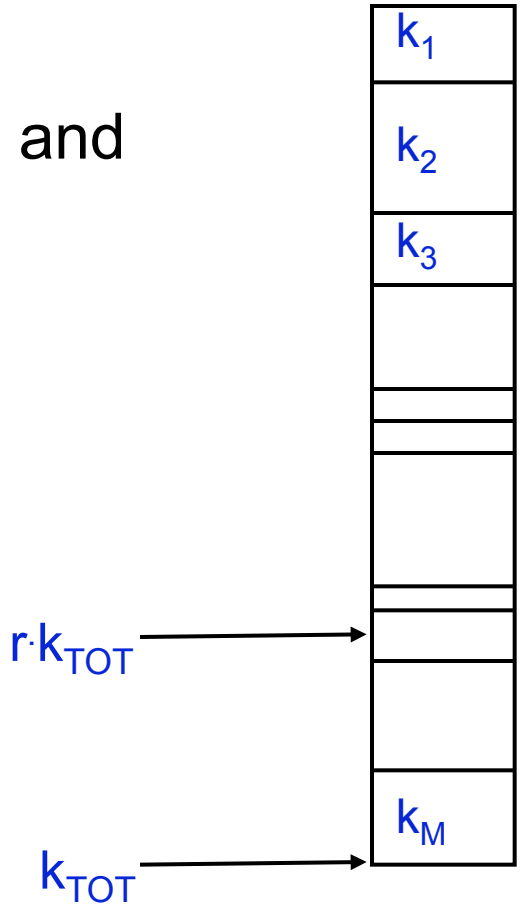
$$p_{AX}(t) = k_{AX}\exp(-k_{AX}t)$$

but only ONE can happen first

Picking an event

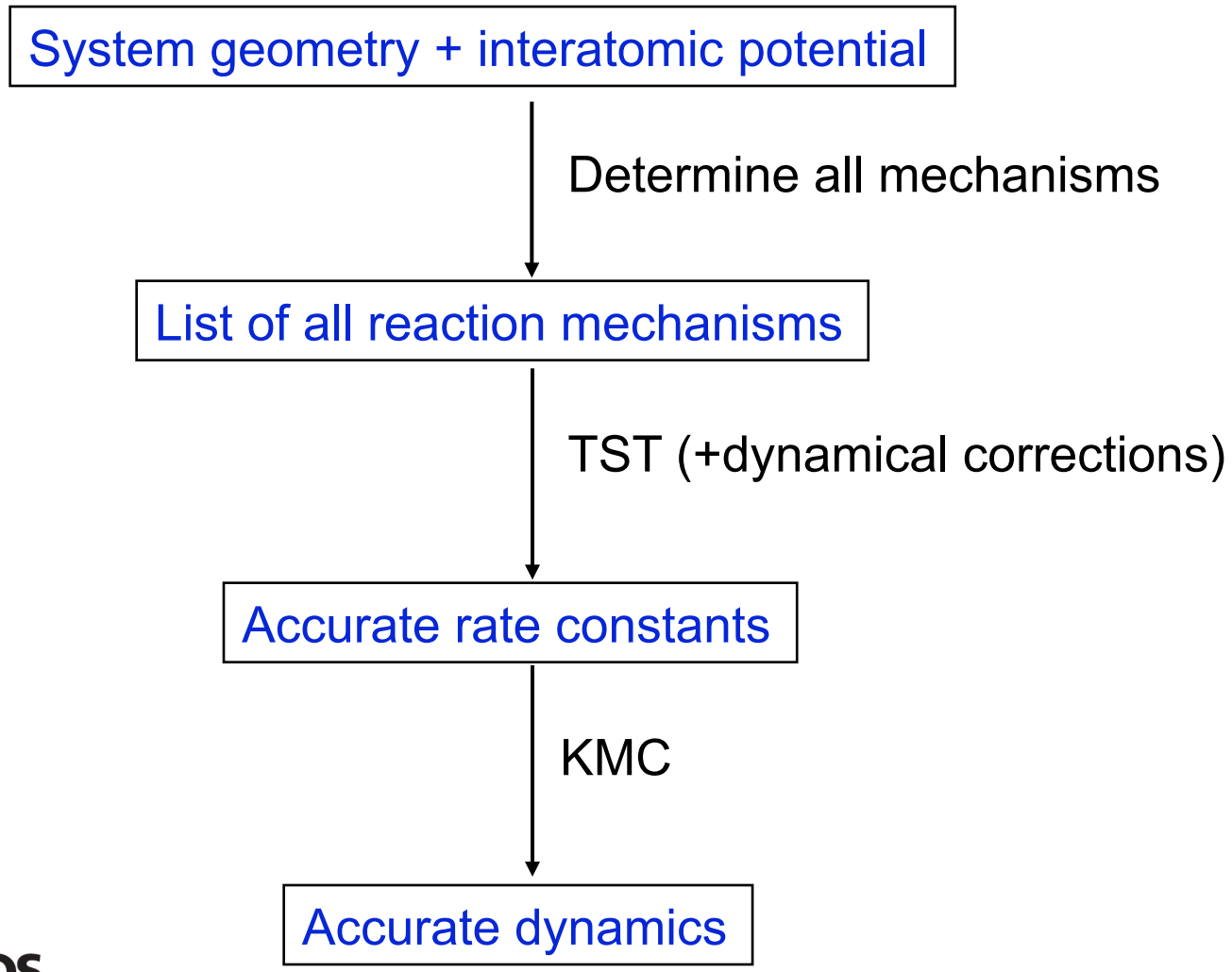
- Put the rate constants “end to end”
- Pick a random number r (on [0,1]) and

  multiply by $k_{TOT} = \sum_{i=1}^{M} k_i$
- See which rate it “hits”



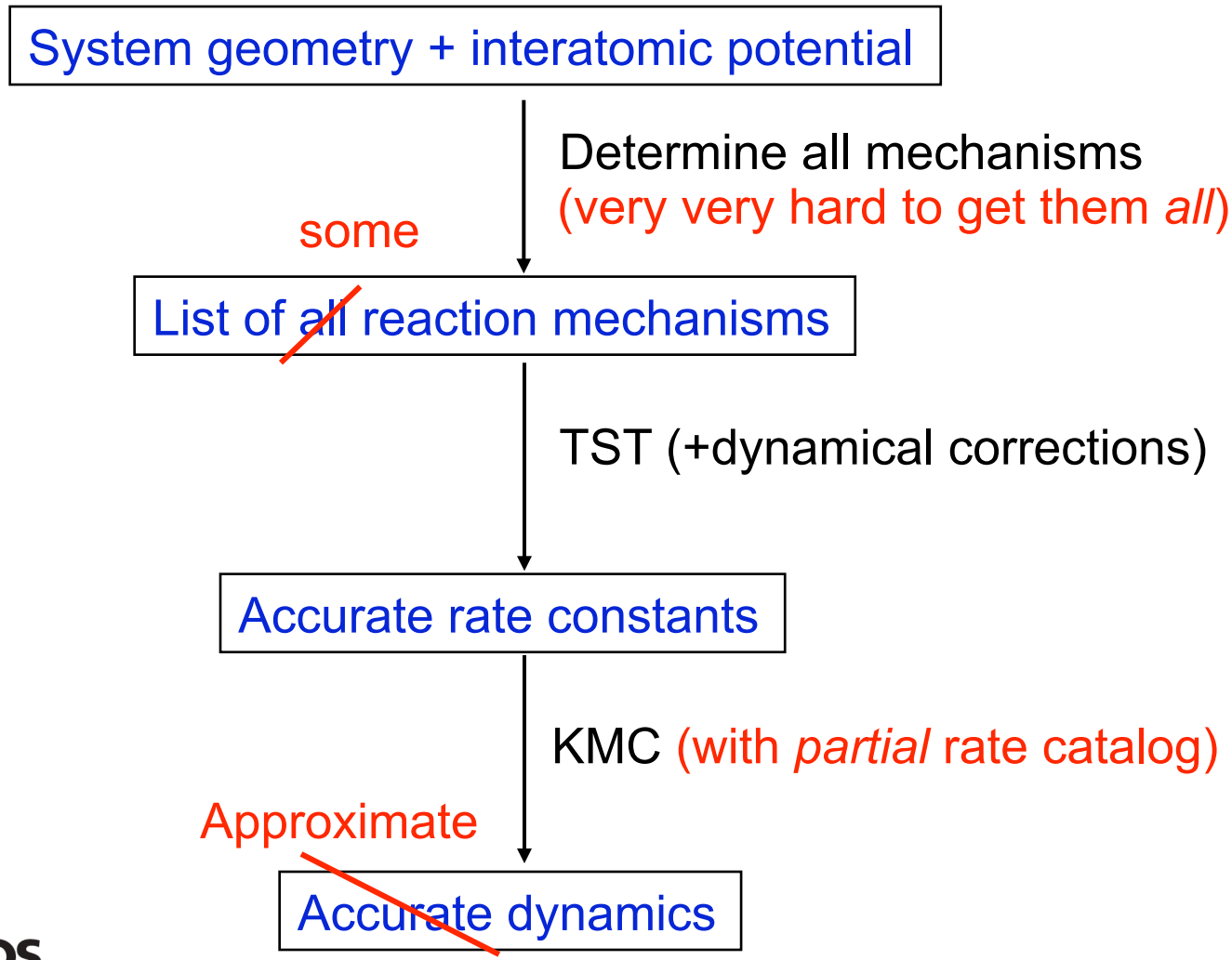
Achievable accuracy of kinetic Monte Carlo

In *principle*:



Achievable accuracy of kinetic Monte Carlo

In *practice*:



Ways to use KMC

Simulation approaches:

- Determine rate constants as accurately and completely as possible; use KMC to push to much longer time scales than MD. Very hard to do right.
- Determine good list of processes without trying to get it perfect; use this as a low-cost approach to reach much longer times.
- Construct simple model and see what you can learn about that type of system. Powerful for qualitative studies.

Inverse-problem approach:

- Construct a (simple) parameterized model; optimize parameter values by iteratively running simulation and comparing predictions to experimental values

What time scale can KMC reach?

- Can afford about ~10^{10} steps.
- Time per step is dominated by fastest event.
- Rates depend exponentially on temperature
- Consequently, the total achievable run time is ***strongly*** system dependent (μs to years!)

Adaptive KMC

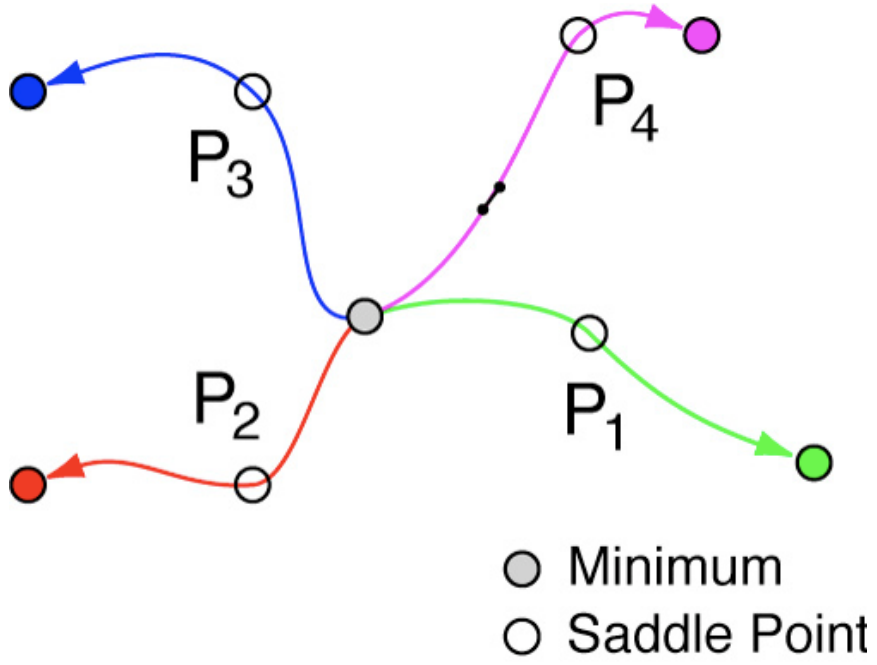
- Combine saddle point searches with KMC

Adaptive Step

1. Find low energy saddles using a min-mode following method

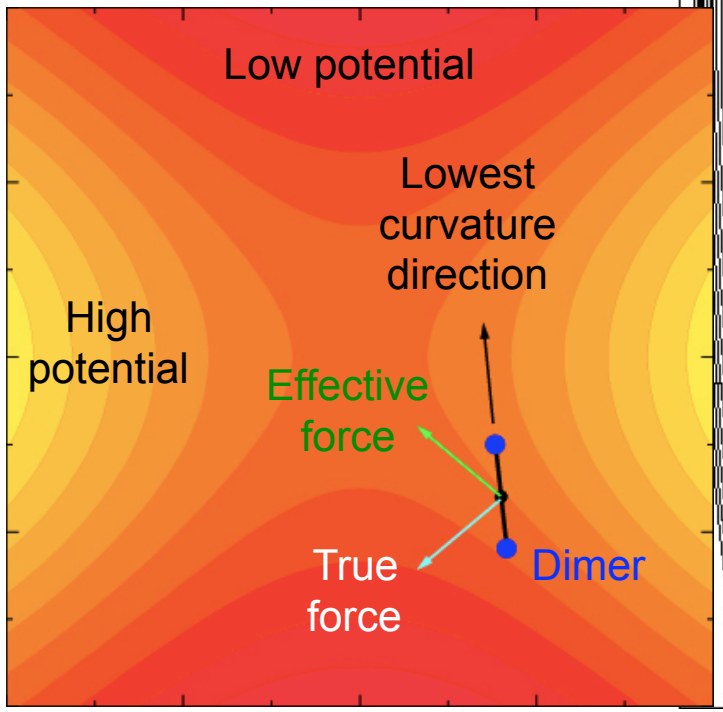
Standard KMC

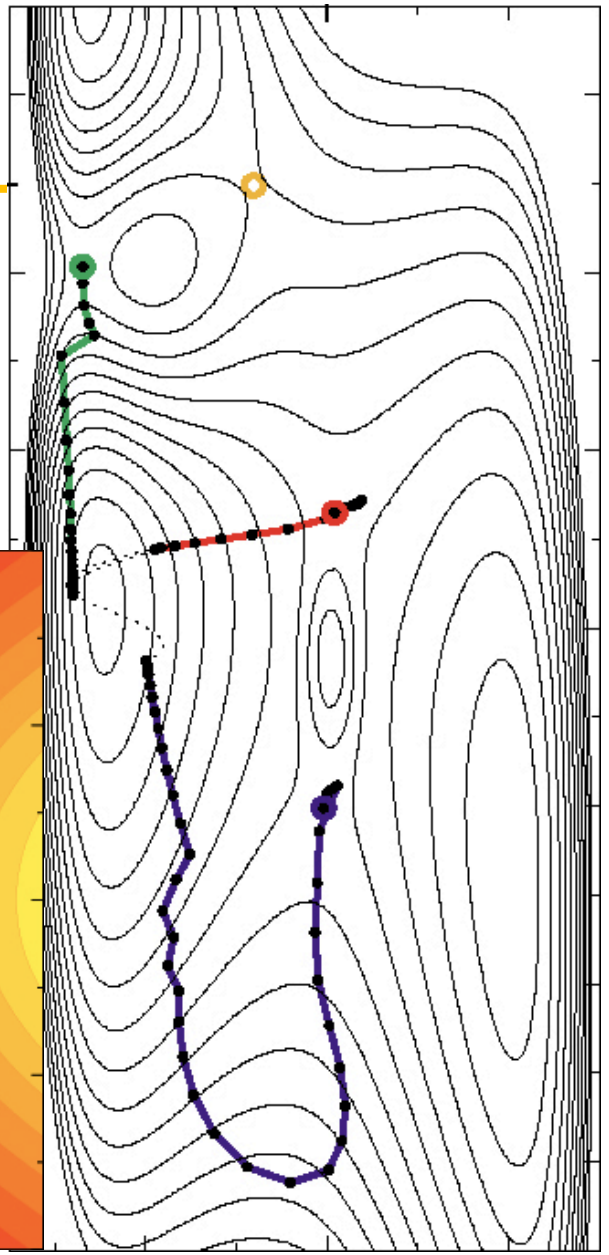
2. Choose one process from a Boltzmann distribution
3. Hop to the final state of the chose process
4. Increment time by an average amount Δt
5. Repeat



Minimum Mode Following

- Find the lowest curvature mode using:
  - Dimer method (Voter, Henkelman, Jonsson)
  - Lanczos (Barkema, Mousseau)
  - Lagrange multiplier (Wales)
- Start from an initial state
- Follow the minimum mode to the saddle
- Independent searches to find multiple mechanisms

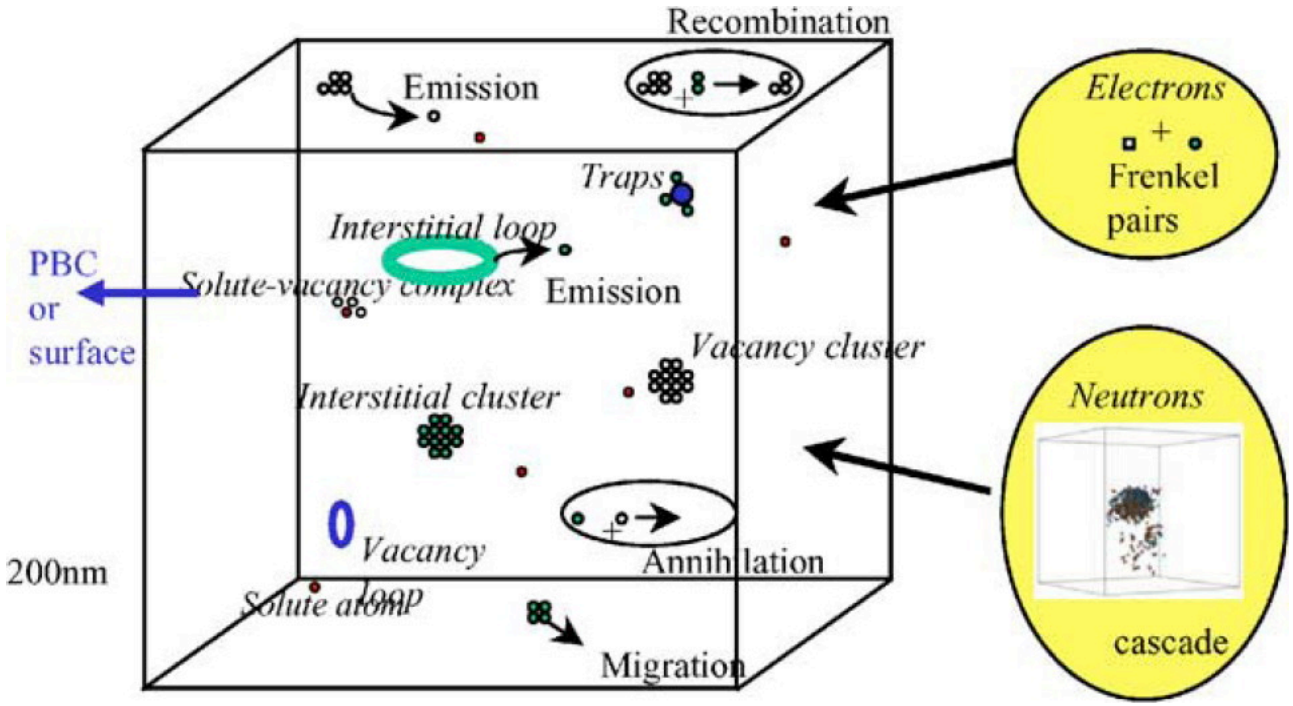




Object kinetic Monte Carlo

- Rather than a fully *atomistic* representation, track the formation, evolution, and interaction of *defects*, such as point defects, point defect clusters, solute atoms, and their sources/ sinks (e.g. surfaces, grain boundaries, or dislocations).

Domain et al, J. Nucl. Mater. **335**, 121 (2004).



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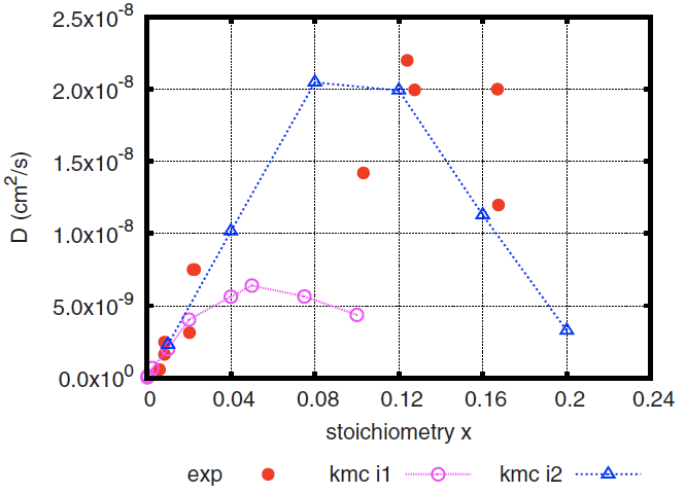
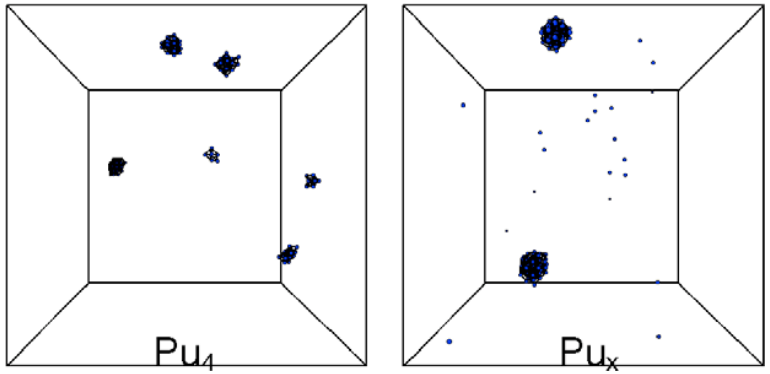
Defect properties that can be simulated with KMC

- Role of competing processes
  - e.g. I_1 vs I_2 vs I_4 in UO_2
- Defect aggregation
- Void mobility/dissociation
- Annealing curves
- Island coarsening
- …



Oxygen transport in UO_2 vs stoichiometry with models based on I_1 vs I_2 mechanism



Vacancy aggregation into voids with two different MEAM potentials for Pu. Basic defect properties from AMD.

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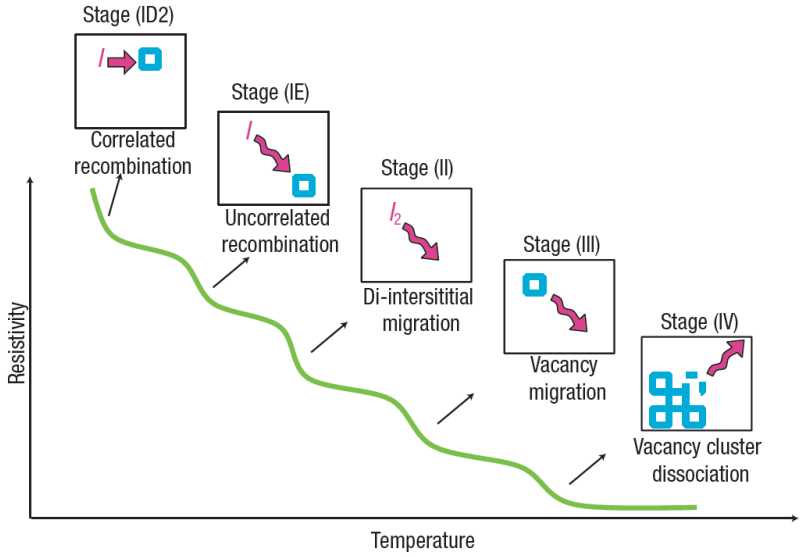
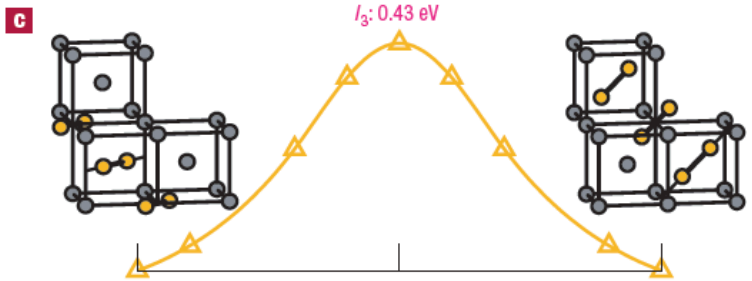
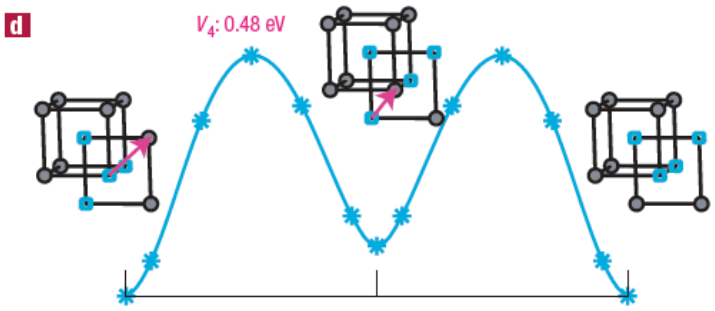
KMC in Radiation Effects Studies: Defect Annealing in Fe

Fu et al, Nat. Mater. **4**, 68 (2005)

- Experimental resistivity measurements reveal a number of annealing stages
- Different stages attributed to different defects
- Calculate defect mobilities (with DFT), feed to KMC



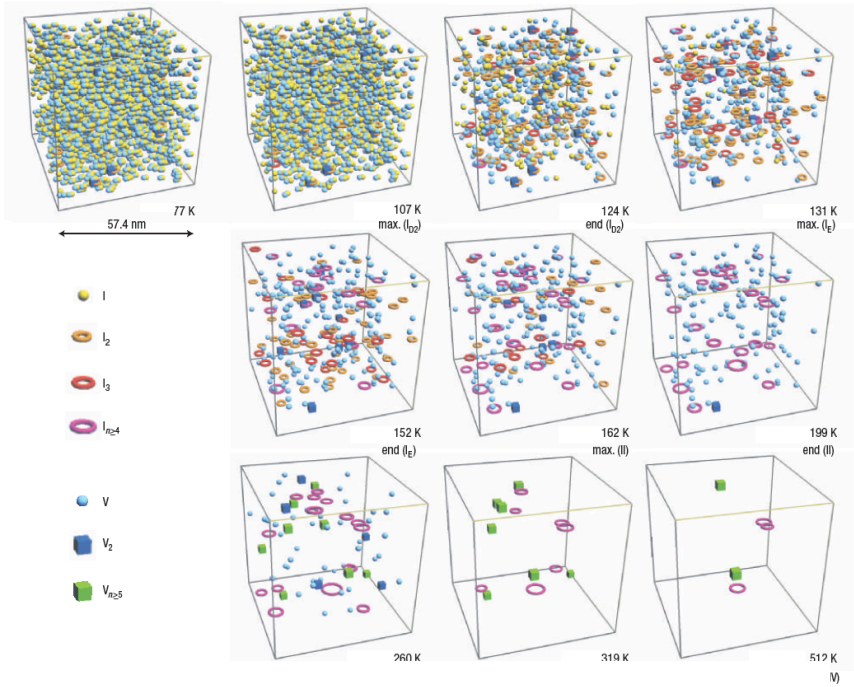


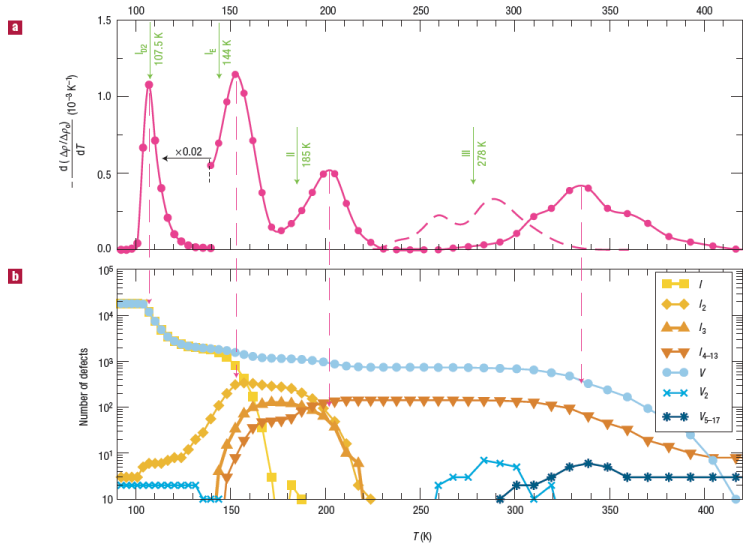


KMC in Radiation Effects Studies: Defect Annealing in Fe

Fu et al, Nat. Mater. **4**, 68 (2005)

- KMC simulation then tracks evolution of defects as a function of time and temperature
- Different annealing stages can then be correlated to specific defects





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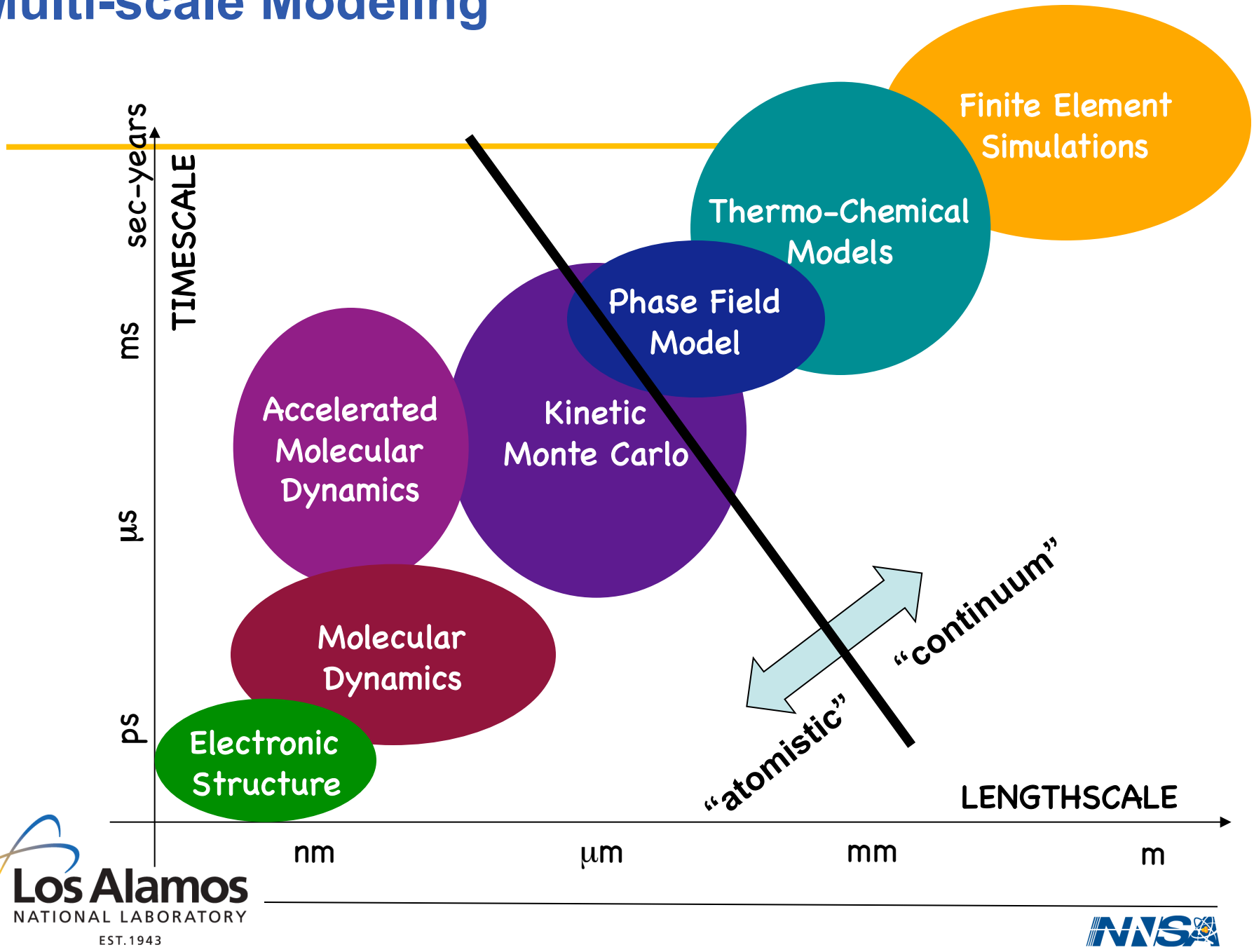
Multi-scale Modeling



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